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(M. S. Thesis)
May 1968

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I. INTRODUCTION

The sintering of particulate solids has been the subject of many investigations both from experimental and theoretical standpoints.\textsuperscript{1-9} The driving force for all sintering is the reduction of surface free energy. Therefore differences in sintering behavior for different systems are the result of different mechanisms of material transport. Sintering is often a complex process, and these mechanisms may depend on many variables. The best understanding of sintering mechanisms has resulted from experimentation with simple systems and the use of models with spherical geometry.

Sintering may occur in the solid state or may be assisted by a liquid phase. Four primary mechanisms for solid state sintering are recognized: evaporation-condensation, surface diffusion, viscous or plastic flow, and volume diffusion. Evaporation-condensation involves the vapor phase transport of material to the neck area between adjoining particles from their outer surfaces. This process obviously requires a significant vapor pressure of the solid material. In addition, this process results in no overall densification but merely the rearrangement of material to give inter-particle bonding.

Surface diffusion, like evaporation-condensation, involves material transfer from particle surfaces to the neck area. In this case, transport is effected by atomic diffusion. This again is merely material rearrangement without densification.

Densification mechanisms in sintering are thus narrowed to two, viscous or plastic flow, and volume diffusion. Detailed models of flow
mechanisms due to the influence of surface tension have been formulated by Clark and White,\textsuperscript{1} and Mackenzie and Shuttleworth.\textsuperscript{2} Both start by assuming viscous flow once an initial stress is exceeded. Rate equations are given indicating that densification rate is inversely proportional to the viscosity coefficient, and the cube of the particle size. Calculated densification curves from these equations substituting suitable values for some parameters are in good agreement with some experimental curves.\textsuperscript{1}

Volume diffusion as a sintering mechanism leading to densification has been studied by Kuczynski,\textsuperscript{3} Kingery and Berg,\textsuperscript{4} and Coble.\textsuperscript{5} The volume diffusion model assumes that sintering proceeds by the migration of vacancies from pores to grain boundaries through the bulk of the material. At the grain boundaries the vacancies are discharged resulting in shrinkage. The rate equations derived from this model again show particle size involved as the inverse cube power. The diffusion model not only gives good agreement with experimental densification curves, but also gives better explanations for other sintering phenomena such as the preferential disappearance of pores near grain boundaries.\textsuperscript{6}

Sintering in the presence of a liquid phase has been studied by Kingery\textsuperscript{7} and others.\textsuperscript{8-10} Systems considered under liquid phase sintering are (1) a pure liquid, (2) a non-reactive solid-liquid, and (3) a reactive solid-liquid. The former two are considered to be similar to the viscous flow model. The most important liquid phase sintering involves the reactive solid-liquid system.

Reactive solid-liquid sintering implies a certain limited solubility of the solid in the liquid. Sintering is markedly affected by
the wetting of the solid phase by the liquid. This liquid phase sintering occurs by solution, diffusion through the liquid, and reprecipitation of the solid. For rapid densification it is essential to have (1) an appreciable amount of liquid phase, (2) an appreciable solubility of the solid in the liquid, and (3) complete wetting of the solid by the liquid. Analysis of the kinetics of this process from the model indicates that the rate of shrinkage is directly proportional to the diffusion coefficient in the liquid phase and to the particle size to the $-4/3$ power.

The necessity for starting materials of small particle size in sintering ceramics is demonstrated in the above discussion. Achieving a small particle size ceramic material is traditionally done by ball milling. The contribution of impurities introduced during ball milling to sintering by the formation of a liquid phase has been largely ignored in sintering studies.

Lead zirconate titanate as one particular ceramic material of considerable importance today has been studied by many investigators. Its piezoelectric properties make it an important transducer material which is used in the manufacture of a wide variety of audio and ultrasonic devices and in many other transducer applications. Lead zirconate titanate (PZT) includes compositions in the solid solution system between lead zirconate (PZ) and lead titanate (PT). Figure 1 shows the low temperature phase diagram for this system. PZT is produced by reacting PbO, ZrO$_2$, and TiO$_2$ between 800-900°C. Experiments have shown that PbTiO$_3$ is first formed; then reacts with ZrO$_2$ and more PbO to form PZT. Typical ceramic processing steps, such as mixing, drying, grinding
(usually ball milling), and cold pressing, are usually present both preceding and following a calcination step. Densification of a powder compact by sintering or hot-pressing follows the powder processing steps.

Research efforts on PZT have concentrated on its electrical properties. Many investigations primarily studying electrical properties of PZT have indicated that higher densities and greater mechanical strength were obtained in samples with impurities purposely added. Additives have long been known to give favorable electrical properties to PZT so that additives are universally employed in commercial production of PZT. Studies have indicated that minor compositional variations in PZT occurring due to variations in fabrication procedure have substantial effects upon densification and subsequent electrical properties of the material.

In the only sintering study of undoped PZT reported in the literature, Iwasa based his determination of the sintering mechanisms on plots of log linear shrinkage vs. log time and vs. reciprocal temperature. It was concluded that volume diffusion is the sintering mechanism for compositions of less than 20 mole% PZ and surface diffusion is the mechanism for those greater than 20 mole% PZ. No consideration is given to the possible role of impurities in this study. As shown previously, surface diffusion has not been considered a mechanism for densification.

It is evident that impurities may contribute significantly to the sintering of PZT and definitely do have an effect on the ultimate electrical properties of the material. Impurities may be added to a material
by intentional doping, or unintentionally during processing steps, such as the ball milling. In order to understand the effects of either of these, first a standard sample should be obtained, alike in all respects except for impurity level to the samples having impurities present. The purpose of this investigation was to make a systematic study of the effect of impurities normally encountered in processing on the sintering behavior and mechanism in the lead zirconate titanate system.
II. EXPERIMENTAL PROCEDURE

A. Powder Preparation

Lead oxide, titanium dioxide and zirconium dioxide were weighed into a glass jar in the proper proportions to make a 400 gram batch of the composition Pb(Zr$_{0.4}$Ti$_{0.6}$)O$_3$. The spectrographic analysis of the oxide raw materials is given in Table I. The oxides were mixed thoroughly with isopropyl alcohol and vacuum dried. The dried powder was then cold pressed into pellets 1 in. in diameter by about 1 in. thick, and calcined in a covered Pt crucible at 800°C for 100 hours. Negligible lead loss occurred in calcining.

The calcined pellets were crushed into powder which had an average particle size according to the Fisher Subsieve Size Analysis of approximately 6-7.5 microns. Some agglomeration of particles might have occurred during calcining making the ultimate particle size smaller than this value. The powder from all calcining batches gave this indicated particle size. X-ray diffraction analysis of every batch indicated only the PZT phase present after calcination.

Approximately 1200 grams of PZT powder were combined from several calcinings to be given one series for ball milling treatments. This powder was divided into four equal batches. One batch was given no further treatment and retained as the control powder ("as calcined" or "unmilled" powder). The other quantities of powder were ball milled (1) dry, (2) in distilled water, and (3) in isopropyl alcohol. High alumina ball mills* with capacity of 1.53 liters half-filled with

* U. S. Stoneware
Table I. Spectrographic Analyses of Oxide Raw Materials

<table>
<thead>
<tr>
<th></th>
<th>PbO (Hammond Lead Products Reagent Grade)</th>
<th>PbO (Baker's Reagent Grade)*</th>
<th>TiO₂ (Fisher's Reagent Grade)</th>
<th>ZrO₂ (Wah Chang Reactor Grade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>.004</td>
<td>.004</td>
<td>.2</td>
<td>.003</td>
</tr>
<tr>
<td>Mg</td>
<td>.0005</td>
<td>.0005</td>
<td>.001</td>
<td>.002</td>
</tr>
<tr>
<td>Fe</td>
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<td>.01</td>
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<td>Al</td>
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<td>.002</td>
<td>.04</td>
<td>.005</td>
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<td>.005</td>
</tr>
<tr>
<td>Cu</td>
<td>.0005</td>
<td>.0005</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ba</td>
<td>.1</td>
<td>&lt;.002</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Bi</td>
<td>.01</td>
<td>.01</td>
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<td>--</td>
</tr>
<tr>
<td>Hf</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>&lt;.025</td>
</tr>
<tr>
<td>Ag</td>
<td>.0005</td>
<td>&lt;.0005</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Nb</td>
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<td>.05</td>
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<td>Ti</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>.005</td>
</tr>
<tr>
<td>Y</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>.006</td>
</tr>
</tbody>
</table>

*Used in later batches to eliminate Ba impurity.
burundum grinding media were used. For the wet milling 180 cc of liquid was used. Ball milling time for all three was 8 hours, and the wet milled powders were dried at 225°F.

Tests performed on these powders included average particle size analysis (Fisher Subsieve Sizer), semiquantitative spectrographic analysis, relative surface areas by nitrogen adsorption (Perkin-Elmer Sorptometer), and x-ray diffraction analysis. The results of the former three are given in Table II and the x-ray analysis indicated no phases present besides the PZT phase.

In order to obtain a powder free of the ball milling impurities, Al₂O₃ and SiO₂, a grinding method was devised utilizing organic materials as the containing material and grinding media. One hundred grams of unmilled powder in a Lucite container with 3/4 in. diameter acrylic spheres was milled dry on a vibratory mill for 10 hours. The resulting powder was given a 12 hour heat treatment in air at 400°C to allow for oxidation of any organic material present. The average particle size of this powder was 1.6-1.8 microns, the same as that obtained for the wet milled powders. The spectrographic analysis of this "plastic milled" powder showed no increase in the inorganic impurity level over that present in the as-calcined powder.

As a fine particle size, high purity material, the plastic milled powder is an ideal standard material for a more detailed study of the effects of Al₂O₃ and SiO₂ impurities on the sinterability of PZT. The addition of varying amounts of these impurities to this material can be done with impurity level as the only variable. Addition of these impurities in solution form was found to be the most satisfactory method.
Table II. Results of tests on Ball Milled and Unmilled Powders

<table>
<thead>
<tr>
<th></th>
<th>As Calcined</th>
<th>Dry Milled</th>
<th>H₂O Milled</th>
<th>Isopropyl Alcohol Milled</th>
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<tr>
<td>I. Semi-quantitative Spectrographic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al* .02</td>
<td>.03</td>
<td>.5</td>
<td>.3</td>
<td></td>
</tr>
<tr>
<td>Si* .01</td>
<td>.02</td>
<td>.18</td>
<td>.08</td>
<td></td>
</tr>
<tr>
<td>Mg* .001</td>
<td>.002</td>
<td>.03</td>
<td>.03</td>
<td></td>
</tr>
<tr>
<td>Fe .02</td>
<td>.02</td>
<td>.02</td>
<td>.02</td>
<td></td>
</tr>
<tr>
<td>Ca .001</td>
<td>&lt;.001</td>
<td>.005</td>
<td>.004</td>
<td></td>
</tr>
<tr>
<td>Cu &lt;.0005</td>
<td>&lt;.0005</td>
<td>&lt;.0005</td>
<td>&lt;.0005</td>
<td></td>
</tr>
<tr>
<td>Bi .003</td>
<td>.003</td>
<td>.003</td>
<td>.003</td>
<td></td>
</tr>
<tr>
<td>Ba .1</td>
<td>.08</td>
<td>.08</td>
<td>.1</td>
<td></td>
</tr>
<tr>
<td>Hf .1</td>
<td>.08</td>
<td>.1</td>
<td>.1</td>
<td></td>
</tr>
<tr>
<td>II. Average Particle Size (μ)</td>
<td>6.4</td>
<td>2.5</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>III. Relative Surface Areas'</td>
<td>1</td>
<td>4.6</td>
<td>8.9</td>
<td>8.1</td>
</tr>
</tbody>
</table>

*Average of two determinations.
Addition of $\text{Al}_2\text{O}_3$ was made by adding appropriate volumes of an aqueous solution of $\text{Al(NO}_3\text{)}_3$ to the powder, mixing the thin slurry ultrasonically, and drying at 110°C. $\text{Al(NO}_3\text{)}_3$ decomposes at about 150°C to form $\text{Al}_2\text{O}_3$. The decomposition thus occurs at too low a temperature to become a factor in the sintering process. Powders prepared by this method contained 0.2, 0.4, 0.6, and 1.2 wt.% $\text{Al}_2\text{O}_3$.

Silica additions using a colloidal silica solution similarly to that for the $\text{Al}_2\text{O}_3$ were made in the amounts 0.2, 0.4, 0.6, 1.2 wt.%.

B. Sample Preparation

Five gram samples from each type of powder were cold pressed at 27,000 psi in a 3/4 in. diam steel die. In order to facilitate handling of the sample prior to firing, 5% of a binder solution was used. The solution used for all powders except the alcohol milled was 2 wt.% stearic acid in 50/50 volume ratio water-ethanol. For the isopropyl alcohol milled powder a 2 wt.% stearic acid solution in isopropyl alcohol was used. The pressed samples were weighed, the heights measured, and marked for identification before being placed into position to be fired.

The typical placement of the samples for firing is shown in Fig. 2. The covering Pt muffle was to minimize PbO vapor loss. The control samples throughout most of the experiments were of the unmilled powder. No significant variation between control samples was noticed. Between the control samples were placed all other types of samples to be fired. The temperature was measured with a Pt-Pt 10% Rh thermocouple.

* Dupont Ludox
The furnace used for sintering the samples and the position of the samples in the furnace are shown in Fig. 3.

A typical sintering run would begin by manual heating to approximately 400°C and holding for one hour to allow for binder oxidation. The furnace was then heated at a constant rate of 400°C/hour to the sintering temperature, held for the specified time (usually 1-1/2 hours), and cooled at a 400°C/hour rate to 800°C. The furnace was then allowed to cool at its natural rate.

C. Measurement Techniques

Bulk densities were determined by means of displacement in mercury. Correction for the temperature variation of the density of mercury was made in the calculations.

Polishing procedure for those samples examined microscopically began with mounting a section of the sample in clear casting resin and polishing on 2/0, 3/0, and 4/0 emery paper. Lapping was then done on a 6 micron diamond impregnated wheel and final polishing followed with a water slurry of either Linde A alumina or cerium oxide. The etchant was a 35% HCl solution with 3 drops of HF per 100 ml of solution.

Polished samples used for electron microprobe analysis were given a carbon coating prior to use. Characteristic Kα lines were used analyzing for Al, Si, and Ti; Lα lines were used for Pb and Zr. The accelerating voltage for the microprobe was 15 kv. Background intensities of Al and Si were obtained from the undoped material.

The scanning electron microscope was used to observe both polished surfaces and as fired surfaces at an electron beam accelerating voltage of 20 kv.
III. RESULTS AND DISCUSSION

A. Investigations of Ball Milled Powders

1. Temperature Dependence of Sintering

The effect of temperature at constant time in the range of 1150-1330°C on the sintered densities of the various prepared powders is shown in Figs. 4 and 5. The powders milled in H₂O and isopropyl alcohol exhibited an optimum range of sintering between approximately 1200 and 1270°C (Fig. 4). Highest densities attained by these air fired samples were slightly above 91% of the theoretical density of 8.0 grams/cc commonly accepted for PZT. The decrease in density at the highest temperature may be attributed to loss of PbO from the surface of the samples at that temperature.

The powder which was ball milled dry and then air fired showed a slight increase in density over the entire temperature range. Much less sintering occurred, the highest density obtained being 78.8% of theoretical (Fig. 5).

The unmilled powder exhibited no sintering whatsoever and in fact lost weight on sintering over the entire temperature range. Cold pressed densities averaged about 70% of theoretical and final densities were mostly below 64%. PbO loss again is evidently the reason for the weight loss. In this case since no sintering occurs PbO loss from the entire free surface may take place over the entire range. The fact that PbO has a vapor pressure of approximately 0.1 atmosphere at 1200°C, and that weight loss increased with temperature support this conclusion. No significant weight loss at temperatures below 1330°C was noticed for the ball milled powders.

The differences in sintering behavior between the wet milled powders and the powders given the other treatments are quite evidently concerned
with the differences in those treatments. Those differences which were measured and are most definite are the particle size and impurity level (Table II). Other differences in materials which might occur due to ball milling, such as those relating to surface properties, are at present difficult to measure and assess. They will be considered to be of secondary importance here. The powders exhibiting greatest sintering (wet milled) were those having the smallest particle size and the highest impurity levels.

All of the proposed sintering mechanisms, as discussed previously, indicate that a small particle size is definitely beneficial to sintering. Impurities were seen to improve many electrical properties of PZT. In this first analysis, impurity level appears to have importance in the sintering process, but the presence of varying particle sizes with varying impurity levels creates uncertainty.

Accompanying the increase in sintering for the ball milled powders, a color change of the fired samples was noticed. All the starting powders and the unmilled fired samples had a light cream coloration. This changed to a light tan for the dry milled samples and a darker tan coloration for the samples from the wet milled powders. This obviously results from the impurity differences, since samples of all types were included in each firing run.

Since this investigation indicated the optimum temperature range for sintering the prepared PZT powder, all further firing was done in the range of approximately 1200-1260°C.

2. Atmosphere Dependence of Sintering

The effect of varying the sintering atmosphere on the resulting sintered density was studied to determine if gas entrapment in pores
during sintering is significant. Coble\textsuperscript{24} found that sintering alumina in air gave lower densities than in oxygen due to gas entrapment.

Sintering runs supplementing those previously done in air were made in argon and oxygen. To accomplish this the furnace was evacuated moderately (to approximately 28 psig vacuum), filled with the gas to be used and re-evacuated. A flow of the desired gas (3-4 ft\textsuperscript{3}/hour) was then established and continued throughout the entire sintering run. The sintering runs were otherwise made as described previously.

It was found that sintering in oxygen resulted in densities nearly three percent higher than for sintering in argon. Air fired densities were intermediate between those for oxygen and argon. Figure 6 shows the relationship between density and the percent of oxygen in the firing atmosphere for samples fired at 1240°C for 1-1/2 hours.

The reason for higher densities in firing in higher oxygen pressures is due to the diffusion of oxygen out of closed pores. This is shown in the microstructures of the oxygen and argon fired samples (Figs. 7 and 8). Oxygen firing gives much smaller pores than does argon firing indicating that argon diffusion out of pores is more difficult than for oxygen. This is understood since argon is the larger atom, and oxygen is widely recognized to have a finite solubility in oxide systems, while argon would not be expected to. The air fired densities are higher than those for argon firing. Air is a mixture of oxygen and nitrogen and apparently nitrogen remains trapped in pores like argon.

A coloration effect was again noticed. The argon fired samples had a light coloration close to that of the starting powder. The color of the oxygen fired samples was a definite brown, darker than the tannish
color of the air fired samples, as noted previously. The colorations of the tan and brownish samples were not as great immediately after firing, but darkened with time at room temperature.

At this point some serious consideration should be given to the possible role of impurities in sintering. Ball milling PZT has introduced $\text{Al}_2\text{O}_3$ and a lesser amount of $\text{SiO}_2$. The possible interaction of these compounds with PZT or its components, the most likely of which is PbO, must be considered. The partial PbO-$\text{Al}_2\text{O}_3$ phase diagram$\text{12}$ shown in Fig. 9 indicates a eutectic high in PbO at $865^\circ$C. The phase diagram, PbO-$\text{SiO}_2$, likewise indicates a low melting eutectic high in PbO below $750^\circ$C. The ternary phase diagram, PbO-$\text{Al}_2\text{O}_3$-$\text{SiO}_2$,$\text{12}$ shows liquidus temperatures as low as $695^\circ$C for compositions as high in PbO as 93 wt.%. Thus, a liquid lead aluminate or lead aluminosilicate must be considered as a possible phase forming in PZT during sintering.

A contribution to the sintering of PZT by such a liquid phase would result if the liquid phase wets the PZT grains at sintering temperatures. A temperature difference between the optimum sintering range (1200-1270°C) and the melting point of the postulated liquid (around $850^\circ$C) is seen. This is probably due to the amount of liquid increasing with temperature and possibly lower viscosity at the higher temperature. Semans$\text{15}$ apparently found no wetting of the PZT grains during hot pressing at $900^\circ$C by a phase assumed to be lead aluminate, although this finding is in question.

At temperatures in the optimum sintering range, the liquid would be expected to have a low viscosity. The fact that a low viscosity wetting liquid leads to sintering which does not change markedly with temperature is suggested by Kingery.$\text{11}$ This is because the major cause of temperature
dependence in liquid phase sintering, the diffusion coefficient in the liquid phase, is relatively constant for a low viscosity liquid.

On cooling down, the liquid phase formed during sintering could crystallize or remain as a glass. As the latter, the darkening of the samples might be expected due to the well known darkening of lead glasses with age.

This investigation involves looking further into the possibility of a liquid phase contribution to the sintering of PZT. Air was chosen as the atmosphere for all further sintering, after having shown the minimal effect of atmosphere and because of convenience.

3. Time Dependence of Sintering

One method often used to study sintering and to determine the sintering mechanism is to consider the general equation for densification during sintering. This is \( \Delta L/L = Kt^y \) where \( L \) = length, \( K \) = constant, \( t \) = time, and \( y \) is an exponent varying with sintering mechanism according to the model accepted. According to this method, a plot of \( \log(\Delta L/L) \) versus \( \log t \) should give a straight line of constant slope \( y \), from which the mechanism can be determined. However, this theory does not always give good results in actual practice.

Sintering runs were performed as described previously except that two samples of each type were used with the unmilled samples being omitted. The dry milled samples were used as control samples. The problem of PbO loss at longer times was anticipated but did not actually present a problem. Weight loss at the longest times was less than 0.5 wt.%. The temperature varied for the different runs between 1199 and 1208°C so that various times could be compared.
The relationship between final density and sintering time is shown in Fig. 10. Relatively rapid sintering is indicated with all but about $3\%$ of the final density attained within one-half hour. All three powders showed only very minor changes in density after 1-1/2 hours of sintering. This indicates that the choice of 1-1/2 hours for the normal sintering time was a good one.

Figure 11 shows a plot of $1/3 \log[(p - \rho_o)/\rho]$, proportional to $\log (\Delta L/L)$, versus $\log t$, where $\rho$ is the final density and $\rho_o$ is the starting density. The straight lines obtained have slopes much less than the predicted values of the exponent $y$ in the general liquid phase densification equation. The rapid sintering at 1200°C resulted in these varying time runs giving data only applicable to the final stages of sintering. The same study conducted at a lower temperature where appreciable sintering first takes place would be expected to produce more meaningful results.

B. Investigation of High Purity Powder

The high purity, fine particle size powder obtained by milling in plastic was used to separate the two variables present in the previous investigations, particle size and impurity level. Sintering runs were made which included samples of the high purity powder along with samples containing various amounts of intentionally added impurities, Al$_2$O$_3$ and SiO$_2$.

A sintering run containing samples with Al$_2$O$_3$ additives in the amounts 0.2, 0.4, 0.6, and 1.2 wt.% added as described previously was made at 1210°C for 1-1/2 hours. The high purity sample was included,
and the control samples were of unmilled powder. Exactly the same procedure was followed for the run made with SiO₂ as an additive. In Fig. 12, the resulting densities are plotted as a function of wt.% impurity. Since the initial particle size is constant, impurity level alone is seen to have an effect of increasing the sintered density. The Al₂O₃ and SiO₂ additives could increase the density by 10% and 5%, respectively. The optimum amount of Al₂O₃ is 0.4 wt.% and of SiO₂ is 0.6 wt.%.

Observations were made on a number of the above samples using the optical microscope, scanning electron microscope and electron microprobe.

The electron microprobe showed that areas of aluminum concentration existed in the Al₂O₃ additive samples. An Al x-ray image of the 0.6 wt.% Al₂O₃ sample is shown in Fig. 14 with the approximate area of the scan indicated on the optical micrograph in Fig. 13. Many Al₂O₃ areas had distinctive appearances like the pore in Fig. 13 at the center left edge of the blocked area. No concentrations of Al other than these characteristic areas could be detected. However, it must be recognized that the microprobe beam diameter is approximately 1-2μ. This is obviously much too large to detect differences at grain boundaries having widths of only a very small fraction of this value. The concentrations of Pb, Ti and Zr were uniform throughout the sample except in areas of high Al concentration where they were decreased, and in areas which fluoresced as discussed below.

Microprobe analysis of SiO₂ as an additive indicated areas of high Si concentration often coincident with areas of high Zr concentration. X-ray images of Si, Zr and Pb are shown in Fig. 15a, b, c for such a sample. The approximate area of the scans in Fig. 15 is indicated in
Fig. 16. In addition to areas of high Si and Zr content, areas of smaller Si concentration were found along grain boundaries and within grains using step scanning techniques. Zr, Ti and Pb counts were much reduced in these areas.

Areas which fluoresced under the electron beam were found in the Al₂O₃ and to a much greater extent in the SiO₂ additive samples. These areas were always coupled with an increase in Zr, and decrease in Pb concentrations. This indicates that areas do exist which are depleted in PbO, and suggests the reaction of PbO with impurities as a definite possibility.

Observations of both Al₂O₃ and SiO₂ additive samples using the scanning electron microscope are shown in Figs. 17-20. Figure 21 shows a sintered sample containing no additive. Examination of the as fired surfaces was most indicative of the nature of the material. For samples containing large pores examination of these was also useful.

The appearances of Figs. 17, 19 and 21 (approximately equal magnification) obviously reflect a great difference in the nature of the various samples. The grain size of the Al₂O₃ additive sample is on the order of 5 microns, whereas for the SiO₂ and no additive samples the grain size is around 20-30 microns. In addition, grains in the Al₂O₃ additive samples are more rounded and have a more equiaxed shape than for the other samples. The grain size difference between Al₂O₃ and SiO₂ additive samples was also found in the interior of the samples by optical microscopy. This is shown in Figs. 13 and 16 from the microprobe optical microscope and more clearly in the photomicrographs of the polished and etched sections in Figs. 22 and 23.
The conclusions to be drawn from the above must first of all be that \( \text{Al}_2\text{O}_3 \) in some form is present at the grain boundaries inhibiting grain growth. The evidence strongly suggests that it is present in the form of a liquid aluminate which wets the PZT grains. The primary function of this liquid is as an aid to sintering but it also inhibits grain growth in the process. The \( \text{Al}_2\text{O}_3 \) which is present in concentrated areas is quite evidently only a minor portion of the total \( \text{Al}_2\text{O}_3 \) present.

One interesting result was obtained from the examination of a polished surface of an \( \text{Al}_2\text{O}_3 \) additive sample using the scanning electron microscope. This was the inability to locate any of the "characteristic" \( \text{Al}_2\text{O}_3 \) concentrations like the one pointed out in Fig. 14. All such areas noticed at lower magnification were in actuality empty pores when examined at higher magnification. Unusual optical reflectance from such pores could possibly explain the light areas observed; however, the reason for high x-ray counts from such areas is not known.

For the \( \text{SiO}_2 \) additive samples, the impurity has a smaller effect upon sintering and has no effect of inhibiting grain growth of PZT. The areas containing small grains as seen in Figs. 19 and 20 are very characteristic of the overall microstructure. These fine grained areas which are probably the result of a devitrification of a silica rich glass correspond to areas like that shown in Fig. 15a, b. They have a composition rich in Si and Zr. The evidence in this case suggests a siliceous liquid sometimes associated with zirconia which does not wet the PZT grains. This liquid is engulfed by growing PZT grains or included at grain intersections and within pores, all of which are represented in Figs. 19 and 20. \( \text{SiO}_2 \) thus appears to play a more passive role in sintering PZT, although the mere presence of a liquid in sintering increases the strength of these samples.
It should be emphasized that the above discussion of wetting and non-wetting liquids is based solely on microstructural observations. The evidence for a wetting aluminate liquid and a non-wetting siliceous liquid is only qualitative until additional experimental evidence is obtained.

The powder of small particle size and no additive does sinter, as shown previously, to approximately 82% of theoretical (later samples of slightly smaller initial particle size to 85%). However, the fired strength of these samples is low compared to the samples containing additives. Samples with no additive were found to be impossible to polish using the usual techniques. This appears to be further evidence supporting a liquid phase contribution to sintering when sufficient impurities are present. The role of the liquid phase after solidification (glassy or crystalline) is obviously to bond the PZT grains together.
IV. SUMMARY AND CONCLUSIONS

Investigations into the effects of ball milling impurities on the sintering of lead zirconate titanate were conducted.

Milling in a plastic container produced a high purity, fine particle size powder. The common ball milling impurities, $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$, were added to this powder in varying amounts. This study of impurity effects in sintering was therefore made with the other major variable, particle size, held constant.

Evidence obtained from the electron microprobe, scanning electron microscope, and optical microscope indicates, in impurity doped samples, the definite presence of a liquid phase at high temperatures which contributes substantially to the sintering of lead zirconate titanate.

Alumina additives increase the sintering by forming a liquid phase which wets the PZT grains. Normal grain growth is reduced by the presence of the aluminate liquid in PZT. Microprobe data suggest lead aluminate is the liquid phase.

Silica additives contribute less to sintering than does alumina. Microstructural observations and microprobe data indicate the formation of a liquid that does not wet the PZT grains. Some reaction of the siliceous liquid with the lead oxide and zirconia of the PZT is indicated by the microprobe data. Silica additions to PZT do not inhibit grain growth.

A minor effect of atmosphere on sintered density was found. Densities obtained by firing in oxygen were about 3% higher than those from firing in argon. This indicates that gas entrapment in closed pores during sintering leads to lower densities.
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Fig. 1  Low temperature PZT phase diagram.\textsuperscript{12}
Fig. 2 Typical arrangement of samples during sintering studies.
Fig. 3 Schematic diagram of furnace.
Fig. 4  Effect of temperature on sintered density of $\text{H}_2\text{O}$ and isopropyl alcohol milled powders.
Fig. 5 Effect of temperature on sintered density of as calcined and dry milled powders.
Fig. 6  Effect of atmosphere on sintered density.
**Fig. 7** Photomicrograph of oxygen fired sample, $\text{H}_2\text{O}$ milled, etched.

**Fig. 8** Photomicrograph of argon fired sample, $\text{H}_2\text{O}$ milled, etched.
Fig. 9  Partial PbO-Al₂O₃ phase diagram.¹²
Fig. 10  Effect of time on sintered density of ball milled powders.
Fig. 11  Log of densification rate vs. log time, ball milled powders.
Fig. 12  Effect of Al₂O₃ and SiO₂ additives to high purity PZT on sintered density.
Fig. 13  Photomicrograph of 0.6 wt.% Al$_2$O$_3$ additive sample showing area of Al x-ray scan (Fig. 14).

Fig. 14  Al $K_{\alpha}$ x-ray image, 0.6 wt.% Al$_2$O$_3$ additive.
Fig. 15  
(a) Si $K_{\alpha}$ x-ray image, 0.6 wt.% SiO$_2$ additive.  
(b) Zr $L_{\alpha}$ x-ray image, 0.6 wt.% SiO$_2$ additive.  
(c) Pb $L_{\alpha}$ x-ray image, 0.6 wt.% SiO$_2$ additive.
Fig. 16 Photomicrograph of 0.6 wt.% SiO$_2$ additive sample showing area scanned in Fig. 15.
Fig. 17 Scanning electron micrograph of 0.4 wt.% Al$_2$O$_3$ additive sample, as fired surface.

Fig. 18 Scanning electron micrograph of 0.4 wt.% Al$_2$O$_3$ additive sample, as fired surface.
Fig. 19  Scanning electron micrograph of 0.4 wt.% SiO$_2$ additive sample, as fired surface.

Fig. 20  Scanning electron micrograph of 0.6 wt.% SiO$_2$ additive sample, interior of pore.
Fig. 21 Scanning electron micrograph of high purity sintered sample (no additive) as fired surface. 700x
Fig. 22 Photomicrograph of 0.6 wt.% $\text{Al}_2\text{O}_3$ additive, sample, etched.

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Fig. 23 Photomicrograph of 0.6 wt.% $\text{SiO}_2$ additive sample, etched.
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