CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 63-59

THE EFFECTS OF SOME FABRICATION CONDITIONS ON THE PROPERTIES OF LEAD ZIRCONATE-TITANATE CERAMICS

by

A. H. WEBSTER

MINERAL SCIENCES DIVISION

COPY NO.

JULY 9, 1963

Mines Branch Investigation Report IR 63-59

THE EFFECTS OF SOME FABRICATION CONDITIONS ON THE PROPERTIES OF LEAD ZIRCONATE-TITANATE CERAMICS

by

A. Hubert Webster[*]

- - -

SUMMARY OF RESULTS

Lead zirconate-titanate ceramic disks suitable for electro-mechanical testing have been fabricated from two lots of mixed lead-zirconium-titanium hydroxide precipitate. The disks were made by cold-pressing and sintering, and the effects of variations in calcination procedure, forming pressure, sintering temperature, and sintering time were investigated. It was found that most of the important variations in electromechanical properties correlated with the densities of the ceramics. The radial coupling factor and the elastic (Young's) modulus increased with increasing density. It appears probable that the dielectric constant and piezoelectric strain coefficient also increase with increasing density. The average properties of ceramic disks produced under the most favourable fabrication conditions were comparable to those properties reported in the literature for similar compositions.

[*] Senior Scientific Officer, Physical Chemistry Section, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

CONTENTS

INTRODUCTION

The properties of a ferroelectric ceramic are determined principally by its chemical composition and crystal structure. The properties of the ceramic may, however, also be affected by such parameters as the bulk density and the microstructure, and,hence,by the fabrication procedures that determine these parameters. The present investigation was undertaken, therefore, to study the effects of variations in fabrication procedure on certain electromechanical properties of polycrystalline lead zirconate-titanate containing a minimum of impurities and without the addition of "doping" agents that are known to modify its properties. This study is a necessary preliminary to the investigation of the effects of variations of chemical composition, since it is important to know what effect necessary or accidental variations in fabrication procedures, bulk density, or grain size will have on the measured properties of the ceramics.

In the lead zirconate-titanate solid solution series there is a morphotropic boundary at about 50 to 55 mol per cent lead zirconate (1, 2, 3). At room temperature the crystal structure near this boundary is of the perovskite type, slightly distorted to rhombohedral symmetry on the $PbZrO_3$ side of the boundary, and slightly distorted to tetragonal symmetry on the $PbTiO_3$ side. The optimum electromechanical properties are found near this boundary, although the extreme values of different properties do not all occur at exactly the same composition (3).

Jaffe et al. (1), in their study of the lead zirconate-lead titanate solid solution, have reported that maximum densities yielded the highest values of radial coupling factor. There appears to be little further definite information available on the relationship between fabrication conditions and the properties of lead zirconate-titanate ceramics formed by the cold-pressing and sintering procedure.

EXPERIMENTAL PROCEDURES

Two lots of coprecipitated hydroxides of lead, zirconium, and titanium, of similar chemical composition, were used as starting materials. The ceramic disks were made by cold-pressing and sintering. On the first lot (17-57) the effects on the properties of the final ceramics of the following variables were investigated: calcination temperature of the precipitate, sintering temperature, and sintering time. On the second lot (17-62) the effects of calcination temperature and forming pressure were investigated, together with a brief study of the effect of sintering time. Evaluation of the electromechanical properties of the ceramics was limited to those parameters most readily measured on samples in the form of circular disks. Selected disks were subjected to chemical analysis, and grain size measurements were made on certain other disks.

(1) Materials

The coprecipitated hydroxides were prepared by Mr. V.M. McNamara of the Extraction Metallurgy Division, Mines Branch. The methods of preparation have been described fully (4). The compositions of the precipitates, are included in Table 2 along with the chemical analyses of the sintered disks.

(2) Outline of Experiments

Three groups of disks were studied. The fabrication variables examined with each group are indicated in Table 1. Group A formed a 3 x 3 x 2 factorial experiment with 2 replications, and Group B formed a 3 x 2 factorial experiment, also with 2 replications. In Group C certain combinations of variables were examined on 2 disks, and other combinations of variables were examined on only one disk.

(3) Fabrication of Disks

Each precipitate was divided into three portions, and each portion was calcined as indicated in Table 1. The precipitates were held at the calcination temperature for 30 minutes in an aluminum oxide container. Subsequently each portion of the precipitate was passed separately through a Trost Jet Mill in order to reduce the particle size. It will be noted that the effects of differences in calcination procedure cannot be separated from the effects of possible differences in milling procedure. Separate experiments, however, have indicated that batches of identical material passed separately through the Jet Mill will sinter to the same density, to within experimental uncertainty.

TABLE 1

Fabrication Conditions Used for Making Ceramic Disks

Precipitate Lot No.	17-57	17-62	
Group	A	B	C

Fabrication Variables	1) Calcination temperature:
	  a) Ppte. not calcined
	  b) 500°C
	  c) 650°C
	2) Sintering temperature:
	  a) 1175°C
	  b) 1200°C
	  c) 1225°C
	
	3) Sintering time:
	  a) 20 min
	  b) 60 min
		1) Calcination temperature:
		  a) Ppte. not calcined
		  b) 650°C
		  c) 750°C
		2) Sintering time:
		  a) 20 min
		  b) 60 min
			1) Calcination temperature:
			  a) Ppte. not calcined
			  b) 650°C
			  c) 750°C
			2) Forming pressure:
			  a) 1.4×10^3 kg/cm^2
			  b) 2.8×10^3 kg/cm^2
			  c) 4.2×10^3 kg/cm^2
			  d) 5.6×10^3 kg/cm^2

Fabrication Constants	Forming pressure: 2.8×10^3 kg/cm^2	1) Forming pressure: 2.8×10^3 kg/cm^2 2) Sintering temperature: 1200°C	1) Sintering temperature: 1225°C 2) Sintering time: 30 min
Number of Disks	36	12	18

Disks were pressed, without binder or other added liquid, from the milled material at the forming pressures quoted in Table 1. An alcohol solution of stearic acid was used as mould lubricant. The disks were set in a zirconia rack with lead zirconate disks on each end of the row. The lead zirconate disks were used to suppress the possible loss of lead oxide. The zirconia rack was placed in an aluminum oxide (Morgan "Purox") tube set in an electrically heated furnace. The disks were heated at 250°/hr in an oxidizing atmosphere to the temperature indicated in Table 1 and held at this temperature for the indicated sintering time. The disks were cooled overnight at the natural cooling rate of the furnace.

The sintered ceramic disks were lapped to give plane parallel faces. Generally the dimensions of the lapped disks were 1.845 cm diameter by 0.150 cm thick, although it was necessary to make a few of the disks smaller than this size. Densities were determined on the lapped disks by weighing and dimensional measurement. Gold electrodes were applied to the faces of the disks by sputtering. In addition, a layer of conductive silver paste was put on top of the gold.

(4) Electromechanical Tests

The disks in Group A were poled under a field of 40 kV/cm for 10 minutes at 100°C; however, because of higher conductivities, the poling of the disks in Groups B and C was limited to a field of 30 kV/cm for 7 minutes at 100°C. The measurements of capacitance, dielectric loss, resonance frequency, and antiresonance frequency used to calculate the electromechanical properties were made about 24 hours after poling. The dielectric constant at 1 kc, the planar coupling factor, Young's modulus, the piezoelectric constants d_{31} and g_{31}, and the dissipation factors under low field at 1 kc and under 1.5 kV/cm at 60 cycles, were determined by standard methods[5] described in detail in reference 6. The value 0.31 was assumed for Poisson's ratio in the calculation of Young's modulus and the piezoelectric constants.

(5) Chemical Analysis

Chemical analyses for Pb, Zr, and Ti were made on selected disks after removal of the electrodes. Lead was determined gravimetrically as the sulphate, zirconium was precipitated with mandelic acid and ignited to ZrO_2, and Ti was determined spectrophotometrically with H_2O_2. Hafnium present was determined and reported with the zirconium. Minor constituents were determined by spectrographic analysis.

(6) Microscopic Examination

Photomicrographs of sections of selected disks were taken at 1000 X magnification. Grain sizes were estimated by drawing two straight lines across each photomicrograph and measuring the diameter of all grains intersected by the lines. Two fields from each section were examined.

(7) X-ray Examination

X-ray powder diffraction patterns were taken on material sampled from two disks, one from Group A and one from Group B. Copper K_α radiation was used with a 114.7 mm diameter camera.

EXPERIMENTAL RESULTS

(1) Chemical Composition of Sintered Disks

The results of chemical analyses on selected disks from Groups A and B (Table 2) indicate that, within the experimental uncertainty indicated by the standard deviations, no systematic changes in composition occur with changes in fabrication conditions over the range of conditions studied. It will be noted that the uncertainties in the analyses of the precipitates, as indicated by the differences between the results for the precipitates "as received" and the results taken from reference 4, are quite large. However, within this uncertainty, the molar ratios of the major constituents in the precipitates are the same as the molar ratios in the sintered disks.

The results of the semi-quantitative spectrographic determinations (Table 3) indicate that the disks were reasonably free from the extraneous elements for which analyses were made.

TABLE 2

Mole Ratios Calculated from Chemical Analyses of Sintered Disks and Precipitates[*]

a) Group A (lot 17-57)

Calcination Temperature	Sintering Time min	Mole ratio $\dfrac{PbO}{ZrO_2 + TiO_2}$		Mole ratio $\dfrac{ZrO_2}{ZrO_2 + TiO_2}$	
		Sintering Temperature - °C		Sintering Temperature - °C	
		1175	1225	1175	1225
Not calcined	20	0.974	0.980	0.530	0.528
	60	0.976	0.978	0.527	0.530
500°C	20	0.975	0.975	0.531	0.526
	60	0.981	0.975	0.528	0.529
650°C	20	0.983	0.973	0.528	0.530
	60	0.982	0.980	0.530	0.530

	$\dfrac{PbO}{ZrO_2 + TiO_2}$	$\dfrac{ZrO_2}{ZrO_2 + TiO_2}$
Mean ratio for disks	0.978	0.529
Standard deviation	0.003_4	0.001_5
Precipitate (as received)	0.974	0.525
Precipitate (ref. 4)	0.999	0.556

b) Group B (lot 17-62)

Calcination Temperature	Sintering Time min	Mole ratio $\dfrac{PbO}{ZrO_2 + TiO_2}$	Mole ratio $\dfrac{ZrO_2}{ZrO_2 + TiO_2}$
Not calcined	20	0.995	0.512
	60	0.998	0.515
750°C	20	1.000	0.512
	60	0.998	0.516

	$\dfrac{PbO}{ZrO_2 + TiO_2}$	$\dfrac{ZrO_2}{ZrO_2 + TiO_2}$
Mean ratio for disks	0.998	0.514
Standard deviation	0.001_1	0.001_1
Precipitate (as received)	0.976	0.511
Precipitate (ref. 4)	1.000	0.534

[*] From Internal Reports MS-AC-63-387 and MS-AC-63-421 by R. Craig.

TABLE 3

Semi-Quantitative Spectrographic Analyses of Sintered Disks[*]

Group A: Lot 17-57

(Sintered 20 minutes at 1200°C)

Calcination Temp of Precipitate	Elements - Per cent						
	Si	Mg	Fe	Ca	Cu	Al	Mn
Not calcined	0.008	Tr?	0.01	0.02	Tr?	0.007	ND
500°C	0.009	Tr?	0.01	0.02	Tr?	0.009	Tr
650°C	0.006	Tr?	0.004	0.02	Tr?	0.009	ND

Group C: Lot 17-62

(Sintered 30 minutes at 1225°C)

Calcination Temp of Precipitate	Elements - Per cent						
	Si	Mg	Fe	Ca	Cu	Al	Mn
Not calcined	0.04	Tr?	0.02	0.02	Tr?	0.01	0.004
650°C	0.04	Tr?	0.02	0.02	Tr?	0.01	Tr
750°C	0.03	Tr?	0.02	0.02	Tr?	0.01	Tr

ND = none detected

Tr = trace: Mg < 0.03, Cu < 0.005

[*] From Internal Report MS-AC-63-453 by E.M. Kranck.

(2) Densities and Structures of the Sintered Disks

The variations in density of the ceramic disks with variations in fabrication conditions are shown in Figures 1 and 2. In accord with previous results (7), it was found that the sintered density increased with increasing sintering temperature and forming pressure. The sintered density also increased with longer sintering times. Calcination of the precipitate 17-62 prior to milling appeared to have little effect on the sintered densities attained. This is in agreement with previous studies on comminuted powders (7). However, calcination appeared to decrease the sintered densities attained from precipitate 17-57; the lowest densities were shown by disks made from precipitate calcined at 500°C[*]. It should be noted that there was a tendency for disks pressed from uncalcined powder to crack during sintering.

Two microstructures are shown in Figure 3. The average grain diameter, as reported in Table 4, did not vary greatly with fabrication conditions. The results for Group A indicate that the grains in pellets fabricated from uncalcined powders are slightly larger than the grains in pellets fabricated from calcined powder, and that the grain size increases slightly with longer sintering time. There is some indication that grain growth is greater in disks fabricated from precipitate 17-62 than in disks fabricated from precipitate 17-57.

X-ray diffraction studies indicated that the crystal structures of the lead zirconate-lead titanate solid solutions formed from both precipitates were rhombohedral. The following lattice parameters, identical within experimental uncertainty, were calculated,

Disk from Group A $\quad a_o = 4.07_2 \quad a = 89°34'$

$\qquad\qquad\quad$ B $\quad a_o = 4.07_1 \quad a = 89°35'$

The crystal density calculated from these parameters is 8.0_1 g/cm^3. There was evidence of a slight trace of monoclinic ZrO_2 in both these samples.

[*] At 500°C calcination was not complete, i.e., some volatile material remained in the powder.
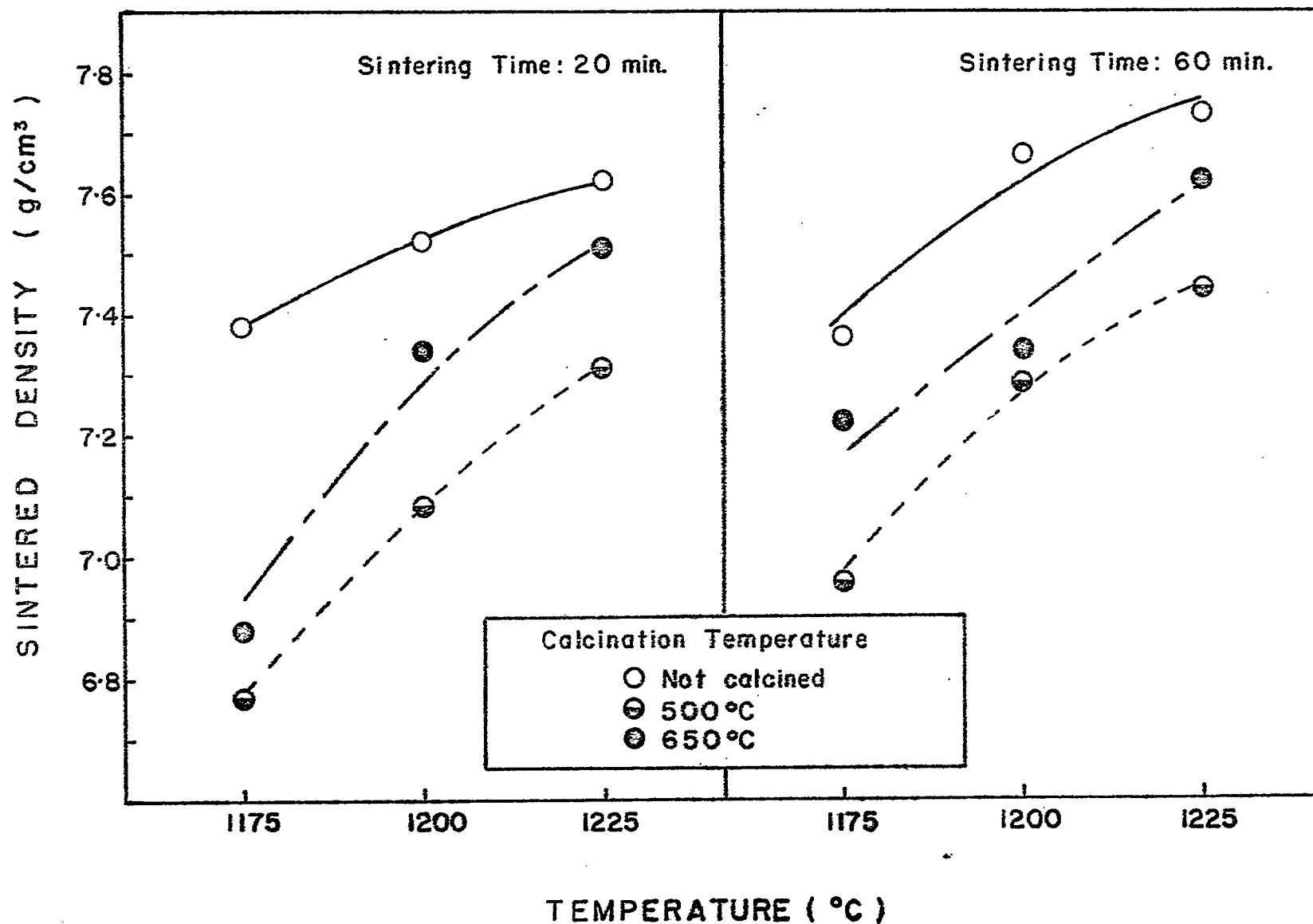
Figure 1. Sintered densities of disks made from precipitate 17-57 (Group A). Each point represents mean density for 2 disks.
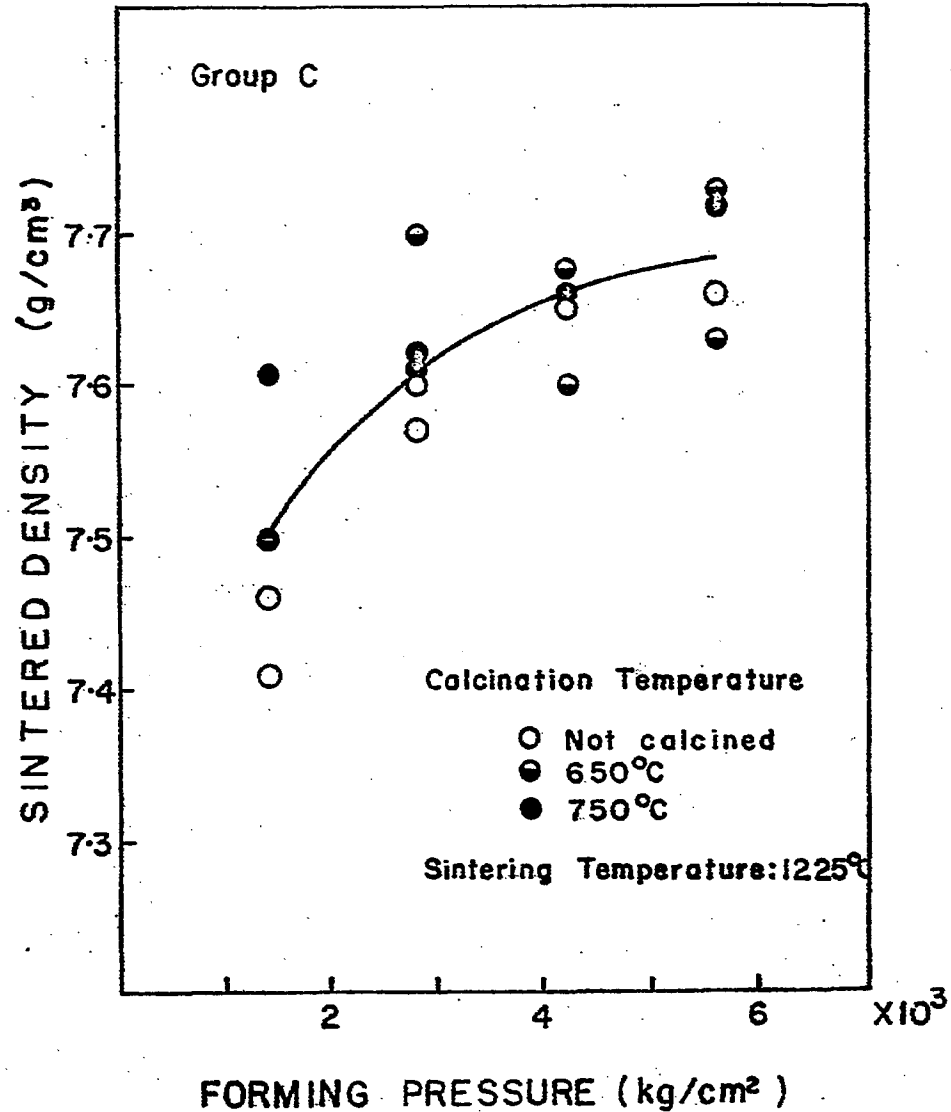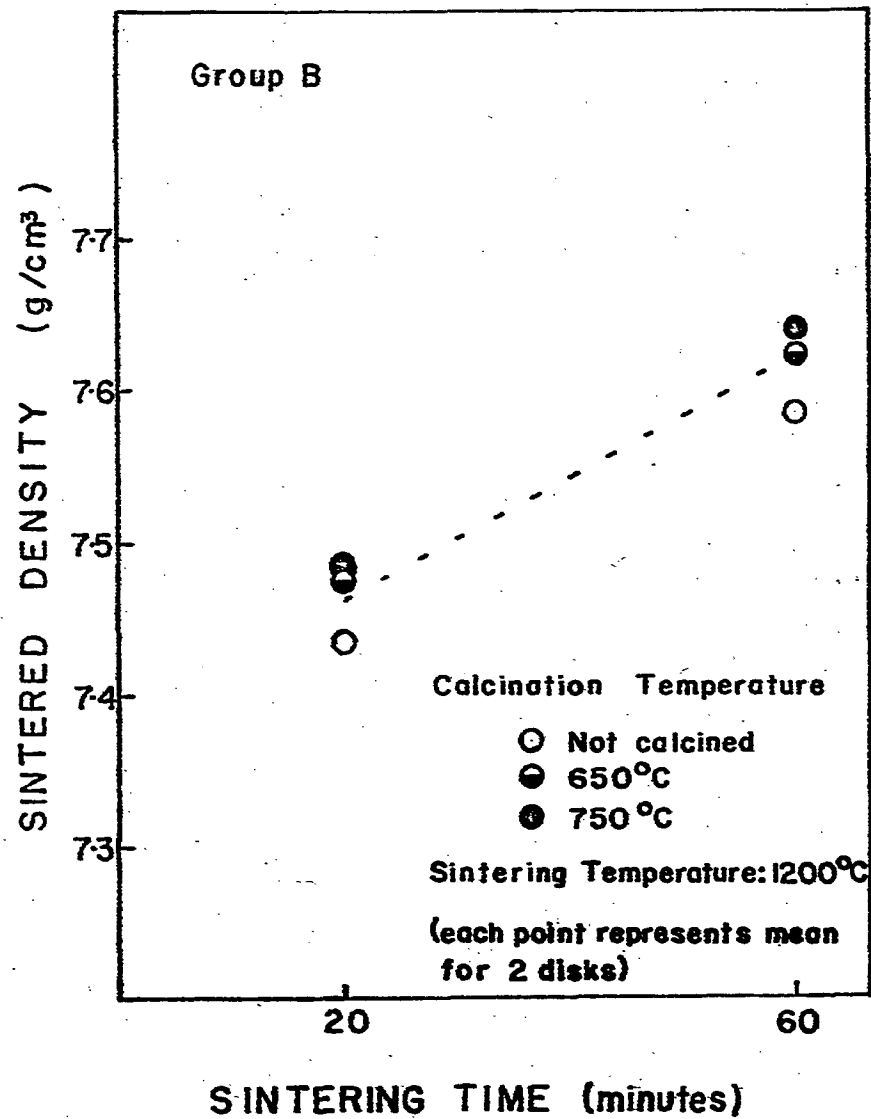
Figure 2. Sintered densities of disks made from precipitate 17-62.

(a) Group A. Disk made from uncalcined precipitate 17-57 and sintered at 1225°C for 60 minutes. Forming pressure 2.8 x 10³ kg/cm².

(b) Group C. Disk made from uncalcined precipitate 17-62. Forming pressure 5.6 x 10³ kg/cm². Sintered at 1225°C for 30 minutes.

Figure 3. Microstructures of lead zirconate-titanate ceramics. Magnification 1000 X. Etched with 1% HCl:0.1% HF.

TABLE 4

Grain Sizes in Sintered Ceramic Disks

(Average grain diameters in microns)

a) Disks from Precipitate Lot 17-57 (Group A)

Sintering Time min	Sintering Temp °C	Calcination Temperature		
		Not calcined	500°C	650°C
20	1175	$4._2$	$2._7$	$2._0$
	1225	$4._2$	$3._2$	$1._8$
60	1175	$4._5$	$3._6$	$3._8$
	1225	$4._4$	$3._3$	$3._7$

b) Disks from Precipitate Lot 17-62 (Group C),
    (Sintered at 1225°C for 30 minutes)

Calcination Temperature	Forming Pressure - kg/cm²	
	1.4×10^3	5.6×10^3
Not calcined	$6._8$	$6._1$
650°C	$5._6$	$6._0$
750°C	$5._2$	$6._0$

(3) Electromechanical Properties

(i) Radial Coupling Factor

It was found that the radial coupling factor, k_p, of the ceramic disks increased with increasing density, as is indicated in Figure 4. Most of the variation in k_p with fabrication conditions could be accounted for by this relationship. The equations of the regression lines plotted in Figure 4 are

$$k_p = 0.45_6 + 0.12_3 \; (\rho - 7.33_5) \quad \text{Group A;}$$

$$k_p = 0.51_9 + 0.10_3 \; (\rho - 7.58) \quad \text{Groups B and C;}$$

where ρ = density in g/cm^3.

The 95% confidence limits on the regression coefficients (the slopes of the above lines) are $\pm 0.02_3$ (Group A) and $\pm 0.03_9$ (Groups B and C). The deviations of observed values of k_p from the above lines did not appear to be a function of grain diameter.

The square of the radial coupling factor is a measure of the efficiency of the conversion of electrical to mechanical energy, or vice versa, when the poled ferroelectric material is used as an electro-mechanical transducer.

(ii) Dielectric Constant

The dielectric constants at constant stress, K_{33}^T, of the poled disks, measured in the polar direction at 1 kc, are plotted in Figure 5 as a function of density. In Group A the dielectric constant appeared to increase with increasing density for a given sintering temperature. However, for a given density, an increase in sintering temperature appeared to produce a decrease in the dielectric constant. The equations of the three regression lines, one for each sintering temperature, were found to be

$$K_{33}^T = 482 + 129 \; (\rho - 7.10) \; \text{Group A, sintering temperature 1175°C;}$$

$$K_{33}^T = 482 + 129 \; (\rho - 7.37) \quad '' \qquad '' \qquad '' \qquad 1200°C;$$

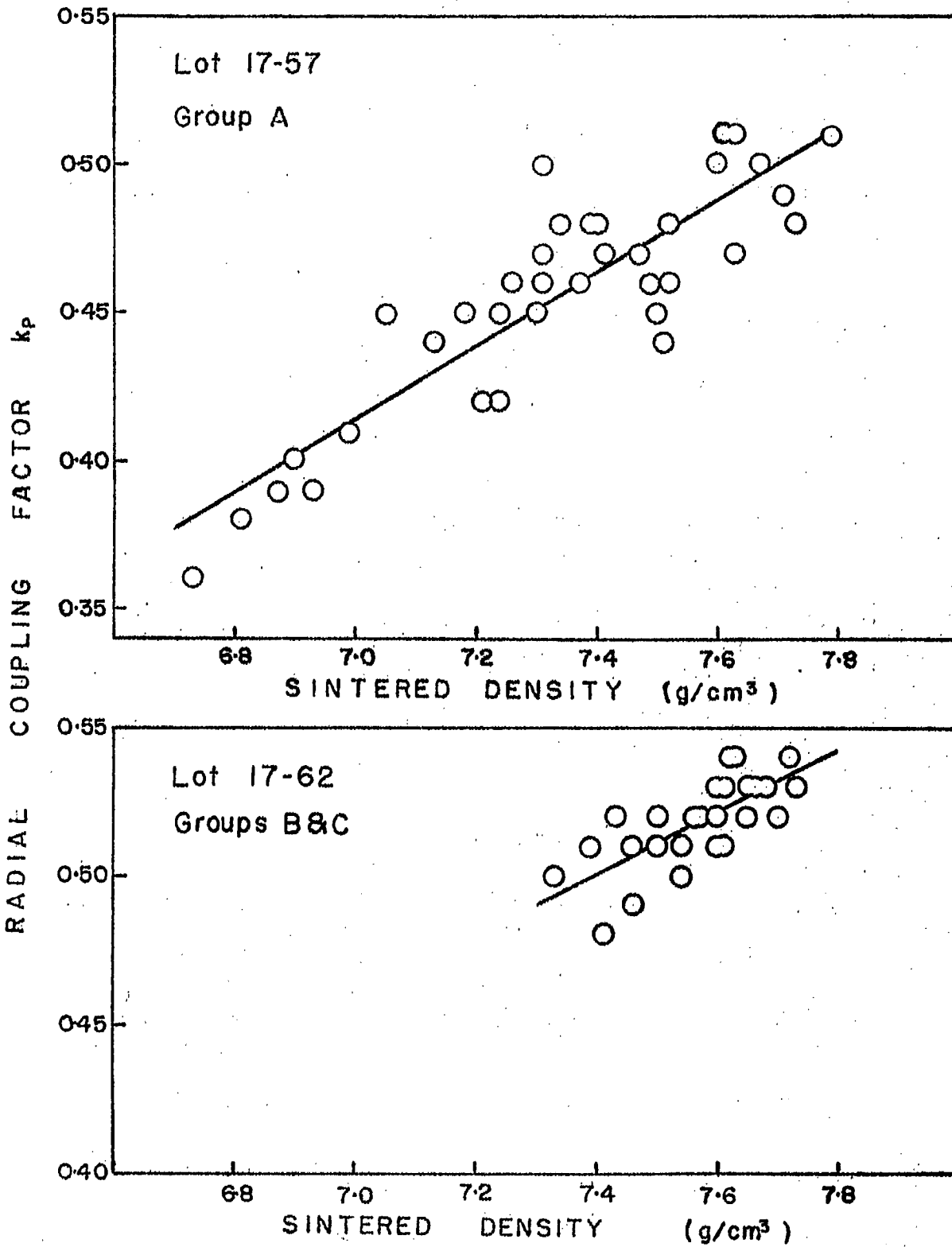$$K_{33}^T = 476 + 129 \; (\rho - 7.54) \quad '' \qquad '' \qquad '' \qquad 1225°C.$$

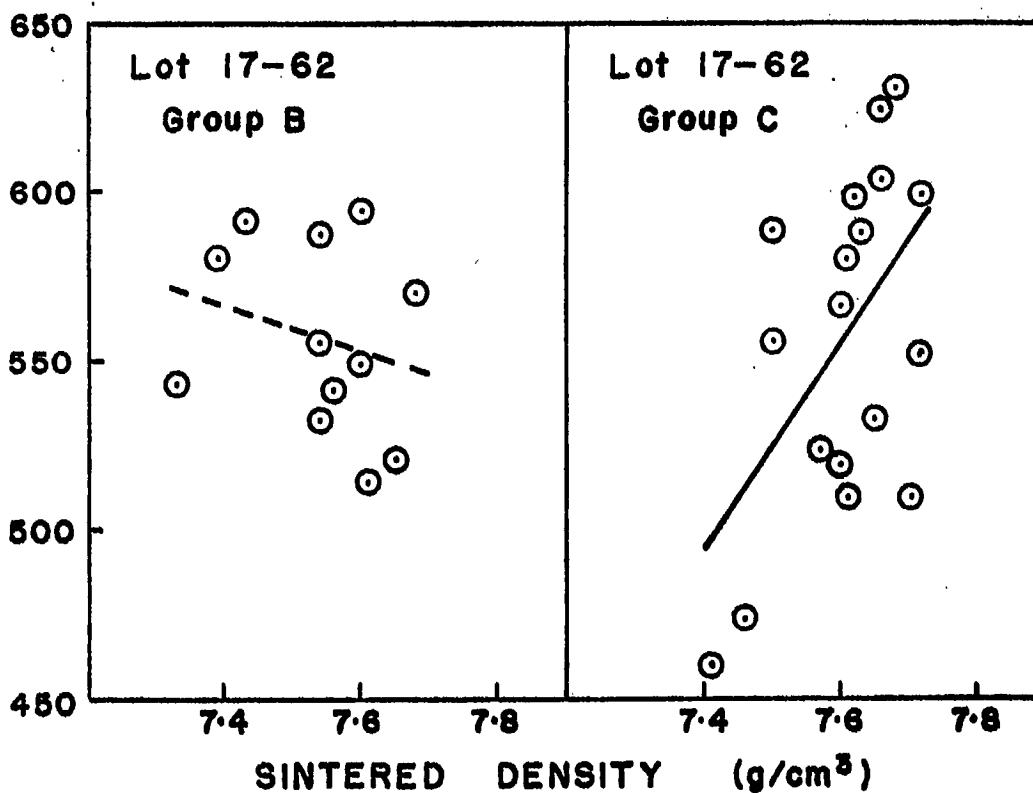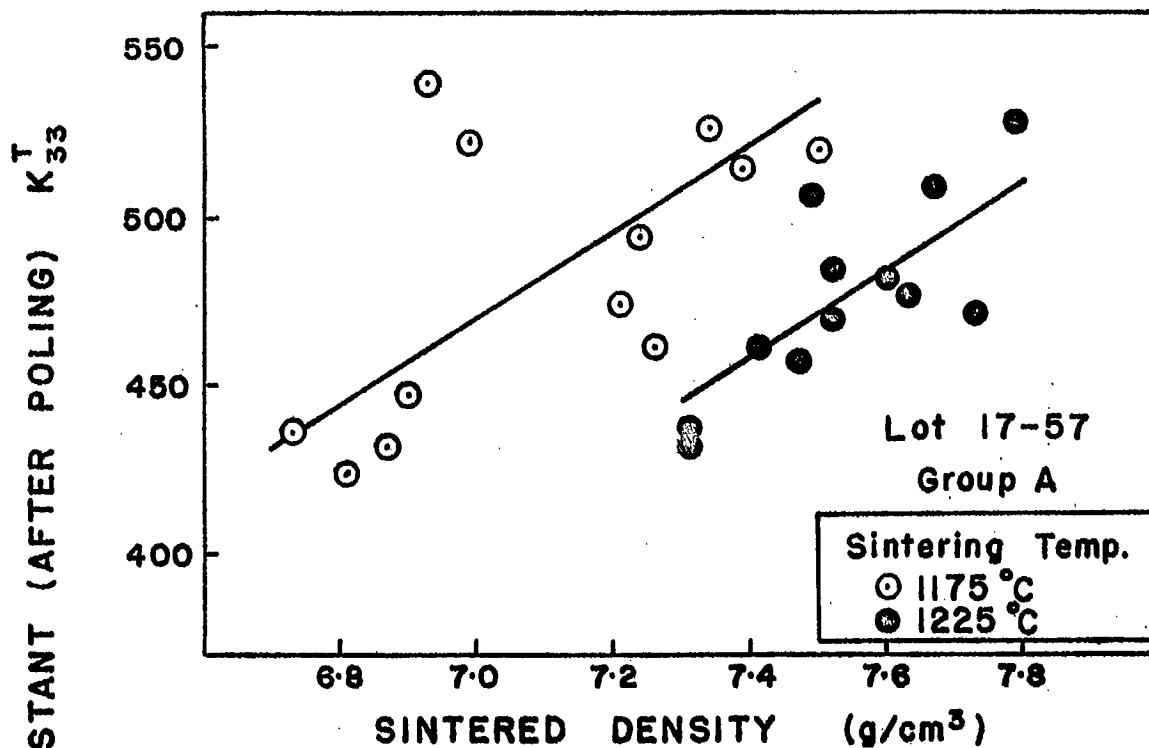Figure 4. Relationship between radial coupling factor and sintered density.

Figure 5. Relationship between dielectric constant (after poling) and sintered density.

The 95% confidence limits on the regression coefficient are $\pm 47^*$. For clarity, only two of these lines are plotted in Figure 5.

Groups B and C involve a smaller number of samples and a more restricted range of densities than Group A. Hence, it is not surprising, considering the relatively large scatter in the results, that little information can be gained on the relationship between K_{33}^T and density,for these two groups.

The grain diameters in ceramics of Group A did not appear to be related to the deviations of individual observations of K_{33}^T from the regression lines given above.

The dielectric constants, K, of the disks, as determined before poling, showed the same dependence upon sintered density as the dielectric constants, K_{33}^T, determined after poling. Comparative values quoted in Table 5 indicate that K is greater than K_{33}^T by about 35% for the compositions under investigation.

(iii) Elastic Modulus

The elastic modulus Y_{11}^E (Young's modulus), at constant field and in a direction perpendicular to the polar direction, increased with increasing sintered density of the ceramic, as indicated in Figure 6. The regression lines were calculated to be

$$Y_{11}^E \times 10^{-10} = 7.83 + 2.78 \, (\rho - 7.33_5) \text{ newton/m}^2, \text{ Group A};$$

$$Y_{11}^E \times 10^{-10} = 7.79 + 2.90 \, (\rho - 7.58) \qquad " \qquad ; \text{ Groups B and C}.$$

The 95% confidence limits for the regression coefficients are ± 0.24 (Group A) and ± 0.47 (Groups B and C).

---

*The results of an analysis of covariance indicated that the regression coefficients were not significantly different (at the 95% level); therefore, the common regression coefficient, 129, is used for the three regression equations.

TABLE 5

Some Electromechanical Properties of Lead Zirconate-Titanate Ceramics Produced from Precipitate Lots 17-57 and 17-62

Note: (1) Uncertainties quoted are standard deviations or standard errors of estimate, (S).
(2) All measurements made at room temperature.
(3) When the density (ρ) is specified, the value for the property is taken from the regression equation. When no density is specified, the value is the mean for all disks in the group.
(4) Sintering temperatures (T) are indicated only for dielectric constants.

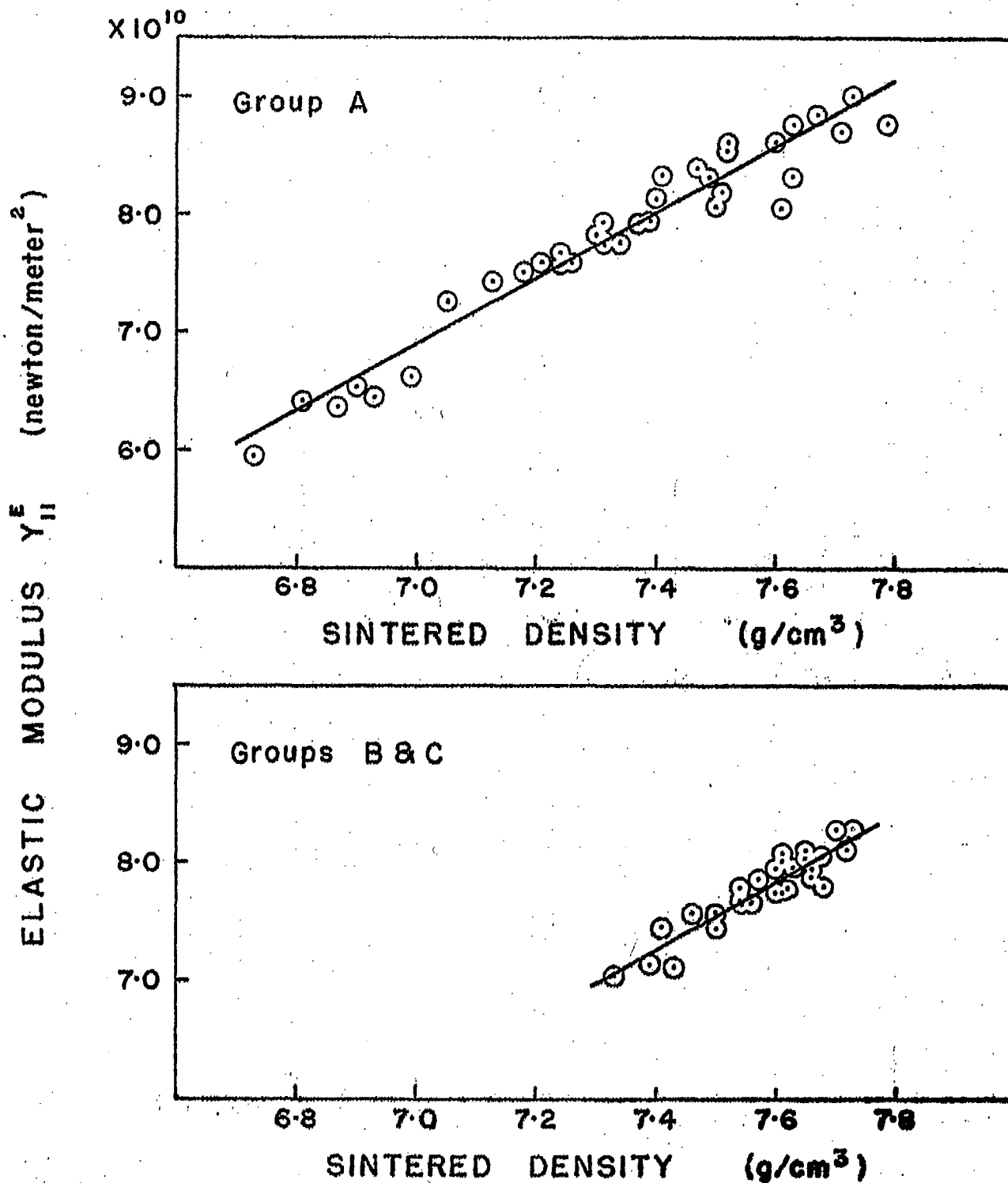| Group	A	B	C
Precipitate Lot No.	17-57	17-62	17-62
Radial Coupling Factor k_p	0.49 ± 0.02 ($\rho = 7.6$ g/cm^3)	0.51 ± 0.01 ($\rho = 7.6$ g/cm^3)	0.52 ± 0.01 ($\rho = 7.6$ g/cm^3)
Dielectric Constant (poled) K_{33}^T	547 (T = 1175°C) 511 (T = 1200°C) 485 (T = 1225°C) ($\rho = 7.6$ g/cm^3) (S = $\pm$ 28)	556 ± 28 (T = 1200°C) ($\rho = 7.6$ g/cm^3)	554 ± 43 (T = 1225°C)
Dielectric Constant (unpoled) K	751 (T = 1175°C) 687 (T = 1200°C) 669 (T = 1225°C) ($\rho = 7.6$ g/cm^3) (S = $\pm$ 40)	not determined	754 ± 43 (T = 1225°C) ($\rho = 7.6$ g/cm^3)
Elastic Modulus Y_{11}^E (newton/meter^2)	$(8.6 \pm 0.2) \times 10^{10}$ ($\rho = 7.6$ g/cm^3)	$(7.9 \pm 0.2) \times 10^{10}$ ($\rho = 7.6$ g/cm^3)	$(7.9 \pm 0.2) \times 10^{10}$ ($\rho = 7.6$ g/cm^3)
Piezoelectric Constant d_{31} (coulomb/newton)	$(64 \pm 2) \times 10^{-12}$ ($\rho = 7.6$ g/cm^3)	$(77 \pm 4) \times 10^{-12}$	$(76 \pm 5) \times 10^{-12}$ ($\rho = 7.6$ g/cm^3)
Piezoelectric Constant g_{31} (meter-volt/newton)	$(14.7 \pm 0.9) \times 10^{-3}$	$(15.6 \pm 0.3) \times 10^{-3}$	$(15.6 \pm 0.4) \times 10^{-3}$
Dissipation Factor tan δ (1.5 kV/cm; 60~) (disks poled)	0.107 ± 0.022 (not calcined) 0.071 ± 0.033 (500°C calcined) 0.040 ± 0.008 (650°C calcined)	0.034 ± 0.003	0.035 ± 0.003
Dissipation Factor tan δ (low field; 1 kc) (disks poled)	$(79 \pm 13) \times 10^{-4}$ (not calcined) $(68 \pm 14) \times 10^{-4}$ (500°C calcined) $(67 \pm 13) \times 10^{-4}$ (650°C calcined)	$(65 \pm 5) \times 10^{-4}$	$(60 \pm 3) \times 10^{-4}$

Figure 6. Relationship between elastic modulus Y_{11}^E and sintered density.

(iv) <u>Piezoelectric Constants</u>

The piezoelectric strain coefficient, d_{31}, appeared to increase with increasing sintered density for disks of Group A, as indicated in Figure 7. The equation of the regression line plotted in Figure 7 is

$$d_{31} \times 10^{12} = 62 + 10.9 \, (\rho - 7.33_5) \text{ coulomb/newton, or meter/volt,}$$

and the 95% confidence limits on the regression coefficient are ± 3.7. As the number of observations and range of densities available with Groups B and C are limited and the scatter of the results is relatively large, no conclusion regarding the variation of d_{31} with density can be drawn for these two groups. Mean values of d_{31} for Groups B and C are quoted in Table 5. The piezoelectric strain coefficient is a measure of the change in polarization produced in the poled ceramic per unit change in stress, or the change in strain produced per unit applied field.

Mean values for the piezoelectric constant $g_{31} = d_{31}/\varepsilon_o K_{33}^T$ (where ε_o = dielectric permitivity of free space, 8.85×10^{-12} farad/meter) as quoted in Table 5. The g_{31} constant indicates the open circuit potential gradient produced by a given applied stress.

(v) <u>Dissipation Factor</u>

The values of the dissipation factor, which indicates the magnitude of the dielectric loss, were determined under two sets of conditions, viz., under a rms field of 1.5 kV/cm at 60 cycles and under low field conditions at 1 kc. The results are summarized in Table 5. It would appear, at least in the case of the high field measurements, that the dissipation factor for Group A decreases with increasing calcination temperature. However, no such variation was observed with the disks produced from precipitate 17-62 (Groups B and C), and an examination of the standard deviations will show that an effect of the magnitude observed with Group A should be clearly evident with Groups B and C also. It would appear, also, that whatever affected the dissipation factors of the disks in Group A did not produce any appreciable effect on the other properties examined. The results on Group A, therefore, are probably anomalous.
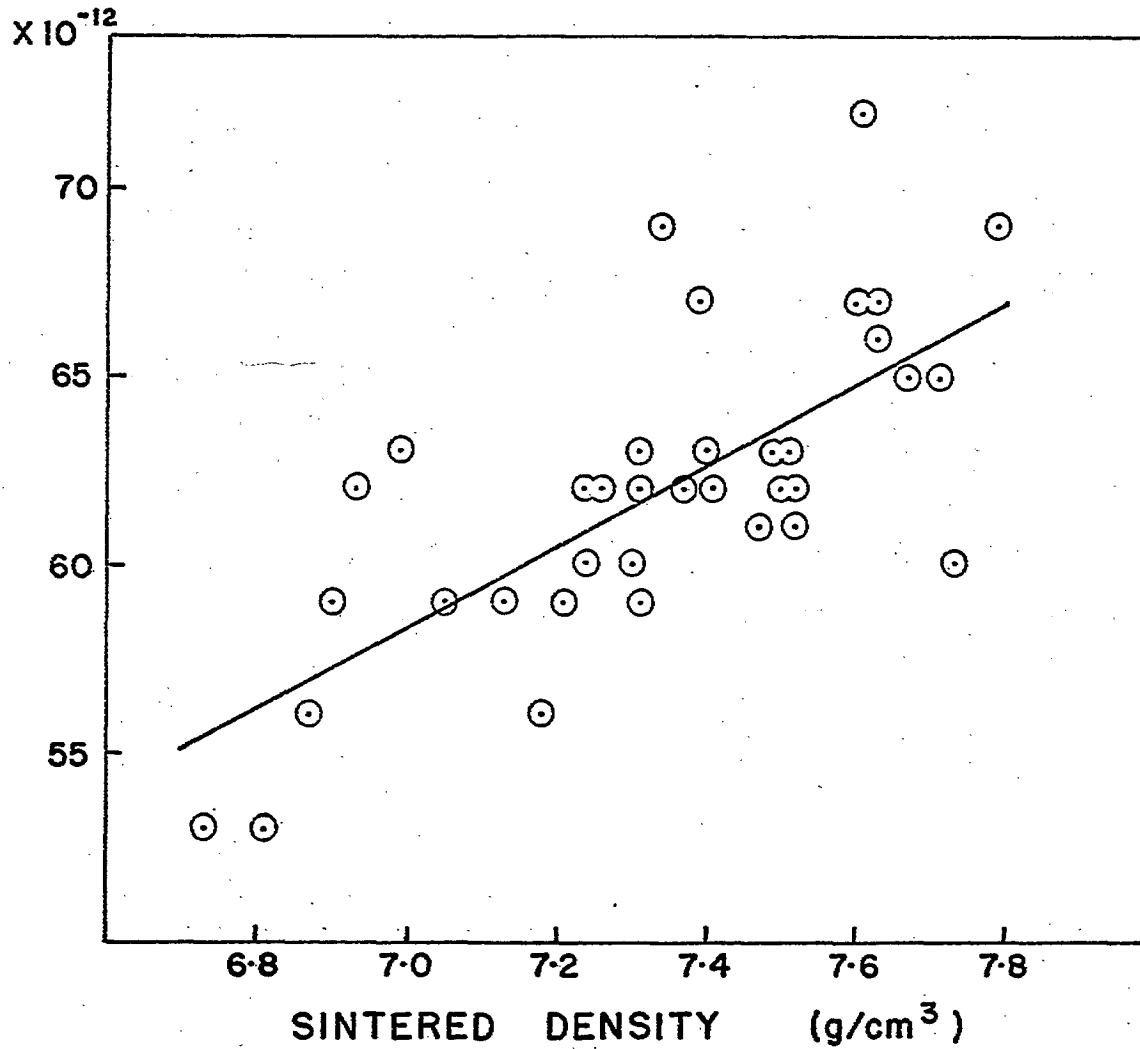
Figure 7. Relationship between piezoelectric strain constant d_{31} and sintered density for disks of Group A.

DISCUSSION

Much of the variation in electromechanical properties associated with variations in fabrication conditions can be attributed to the differences in densities attained under the different fabrication conditions. The residual scatter remaining after the effect of density has been taken into account is indicated by the standard errors of estimate quoted in Table 5. This residual scatter could not be correlated with changes in grain size among the specimens.

The Young's modulus of a sintered ceramic material is known to decrease with increasing porosity of the ceramic (8, 9)[*]. However, no simple quantitative treatment is applicable to this phenomenon, since the exact dependence of the elastic modulus on porosity can vary with the type of material (9). Qualitatively, then, the increase in the elastic modulus with increasing density reported in the present work is to be expected. Qualitatively, also, a decrease in dielectric constant with increasing porosity is to be expected, since, in a given volume of sample, the solid of high dielectric constant is partially replaced, as the density decreases, by voids of $K \sim 1$. A dependence of dielectric constant on the porosity of $BaTiO_3$ was noted by Egerton and Koonce (10).

The radial coupling factor and piezoelectric strain constant are related by the expression,

$$ k_p = d_{31} \sqrt{\frac{2 Y_{11}^E}{\varepsilon_0 K_{33}^T (1 - \sigma^E)}} \, , $$

where σ^E = Poisson's ratio (assumed to be constant).

Hence, variations of k_p, d_{31}, Y_{11}^E and K_{33}^T with density are interdependent.

It is not clear why there should be an apparent decrease in dielectric constant with an increase in sintering temperature for disks of a given density. This decrease does not seem to be related to a change in grain size or to a shift in chemical composition.

---

[*] If only one phase is present in the ceramic, % porosity $p = (\frac{\rho^0 - \rho}{\rho_0}) \times 100$, where ρ^0 = crystal density. The proportion of second phase in the samples being considered in this report is very small.

The chemical compositions of the sintered disks, as given by the molar ratios of the major constituents, did not depend on the fabrication conditions used. The composition of the perovskite-type phase in the Group A disks was estimated, from the results of chemical analysis, to be $Pb(Zr_{0.518}Ti_{0.482})O_3$ with 0.023 mole zirconia in excess per mole of perovskite-type phase. The composition of Group B disks would be $Pb(Zr_{0.514}Ti_{0.486})O_3$, as indicated directly by the analysis.

The variations in grain size in the ceramics of Group A produced by variations in the firing conditions were relatively small and did not appear to have an appreciable effect on the properties of the ceramics. Excessive grain growth, however, might produce noticeable changes in properties.

It should be noted that the conclusions drawn from this investigation apply only to the range of fabrication conditions studied and to the type of precipitate used as starting material.

It should also be noted that the present study was made on samples of "unmodified" lead zirconate-titanate (i.e., lead zirconate-titanate without additions of other oxides such as Nb_2O_5 or SrO). Also, although the compositions were near the morphotropic boundary, they may not have included the composition giving the optimum electro-mechanical properties.

A comparison between some of the present results and previously reported values of the electromechanical properties of lead zirconate-titanate solid solutions is presented in Table 6. The values quoted for the investigations of Berlincourt et al. (3) and Weston (11) were obtained by interpolation of the figures reported. It is seen that property values obtained in the present study are, in general, comparable to those given by Berlincourt, except that the values of K_{33}^T are somewhat lower. The results quoted in reference 11 are based on a comparatively small number of samples made from pneumatically-milled oxides, and it appeared that a shift in chemical composition towards lower zirconate/titanate ratios occurred during processing. There is no doubt that better electromechanical properties and a higher degree of chemical stability were attained in the present investigation.

TABLE 6

Comparison of Present Results with Previously Reported Properties
of Lead Zirconate-Titanate

x in $Pb(Zr_x Ti_{1-x})O_3$	0.51_4			0.51_8		
Investigation	Present*	Berlincourt et al. (3)	Weston (11)	Present*	Berlincourt et al. (3)	Weston (11)
K^T_{33}	555	790	900	500	730	950
k_p	0.52	0.49	0.38	0.49	0.51	0.40
d_{31} coulomb/newton	76×10^{-12}	90×10^{-12}	70×10^{-12}	64×10^{-12}	96×10^{-12}	76×10^{-12}
g_{31} meter-volts/ newton	15.6×10^{-3}	12.3×10^{-3}	8.7×10^{-3}	14.7×10^{-3}	13.6×10^{-3}	8.9×10^{-3}

*Data taken from Table 5.

ACKNOWLEDGEMENTS

REFERENCES

1. B. Jaffe, R.S. Roth, and S. Marzullo, "Properties of Piezoelectric Ceramics in the Solid-Solution Series Lead Titanate-Lead Zirconate-Lead Oxide: Tin Oxide and Lead Hafnate", J. Res. Nat. Bur. Stds., 55, 239 (1955).

2. G. Shirane and K. Suzuki, "Crystal Structure of $Pb(Zr-Ti)O_3$", J. Phys. Soc. Japan 7, 333 (1952).

3. D.A. Berlincourt, C. Cmolik, and H. Jaffe, "Piezoelectric Properties of Polycrystalline Lead Titanate Zirconate Compositions", Proc. IRE 48, 220 (1960).

4. V.M. McNamara and W.A. Gow, "A Chemical Precipitation Method for the Production of a Homogeneous, High Purity Powder Applicable to the Lead Zirconate Titanate Solid-Solution Series", Mines Branch Investigation Report IR 63-39, Department of Mines and Technical Surveys, Ottawa, (1963).

5. IRE Standards on Piezoelectric Crystals, 1961, Proc. IRE 49, 1161 (1961).

6. T.B. Weston, "Electromechanical Properties of Three Experimental
    Lead Zirconate-Lead Titanate Ceramic Compositions",
    Mines Branch Research Report R 100, Department of Mines
    and Technical Surveys, Ottawa (1962).

7. A.H. Webster, "The Sintering Characteristics of Precipitated Mixed
    Hydroxides of Lead, Zirconium, and Titanium", Mines Branch
    Investigation Report IR 62-45, Department of Mines and
    Technical Surveys, Ottawa (1962).

8. R.L. Coble and W.D. Kingery, "Effect of Porosity on Physical
    Properties of Sintered Alumina", J. Amer. Ceram. Soc.,
    39, 377 (1956).

9. S. Spinner, F.P. Knudsen, and L. Stone, "Elastic Constant-Porosity
    Relations for Polycrystalline Thoria", J. Res. Nat. Bur. Stds.
    67C , 39 (1963).

10. L. Egerton and S.E. Koonce, "Effect of Firing Cycle on Structure and
    Some Dielectric and Piezoelectric Properties of Barium
    Titanate Ceramics", J. Amer. Ceram. Soc., 38, 412 (1955).

11. T.B. Weston, "Electromechanical Properties of Some Piezoelectric
    Ceramics Produced from Pneumatically Milled Powders",
    Mines Branch Investigation Report IR 62-61, Department of
    Mines and Technical Surveys, Ottawa (1962).

- - - -

AHW:DV

ELECTRONIC CERAMICS

ECRDC RESEARCH PROJECT C 73

Identification of Mines Branch Personnel

Advisory Committee

Ian F. Wright, MPD*, Chairman
W.A. Gow, EMD
Dr. N.F.H. Bright, MSD
Mr. J.G. Brady, MPD
Mr. V.A. McCourt, N

Operational	Function
Mr. V.M. McNamara, EMD	Pilot plant ceramic powder preparation
Mr. J.C. Ingles, EMD	Control analyses
Dr. A.H. Webster, MSD	Sintering and structural studies
Mr. V.A. McCourt, N	Lapidary and electroding
Mr. Ian F. Wright, MPD	Ceramic engineering
Mr. T.B. Weston, MPD	Electronic test methods and component evaluation
Mr. W.R. Inman, MSD	Wet chemical analytical methods and analyses
Dr. A.H. Gillieson, MSD	Spectrographic analyses
Dr. M.H. Haycock, MSD	Sample preparation for petrographic studies

*MPD – Mineral Processing Division
EMD – Extraction Metallurgy Division
MSD – Mineral Sciences Division
N – Naval Section

Ian F. Wright,
Project Co-ordinator

John Convey,
Director, Mines Branch.