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LEAD ZIRCONATE TITANATE (LZT) CERAMICS.(U)
AUG 79 J H ROSOLOWSKI, R H ARENDT   N00014-76-C-0659
UNCLASSIFIED   SRD-79-123   NL

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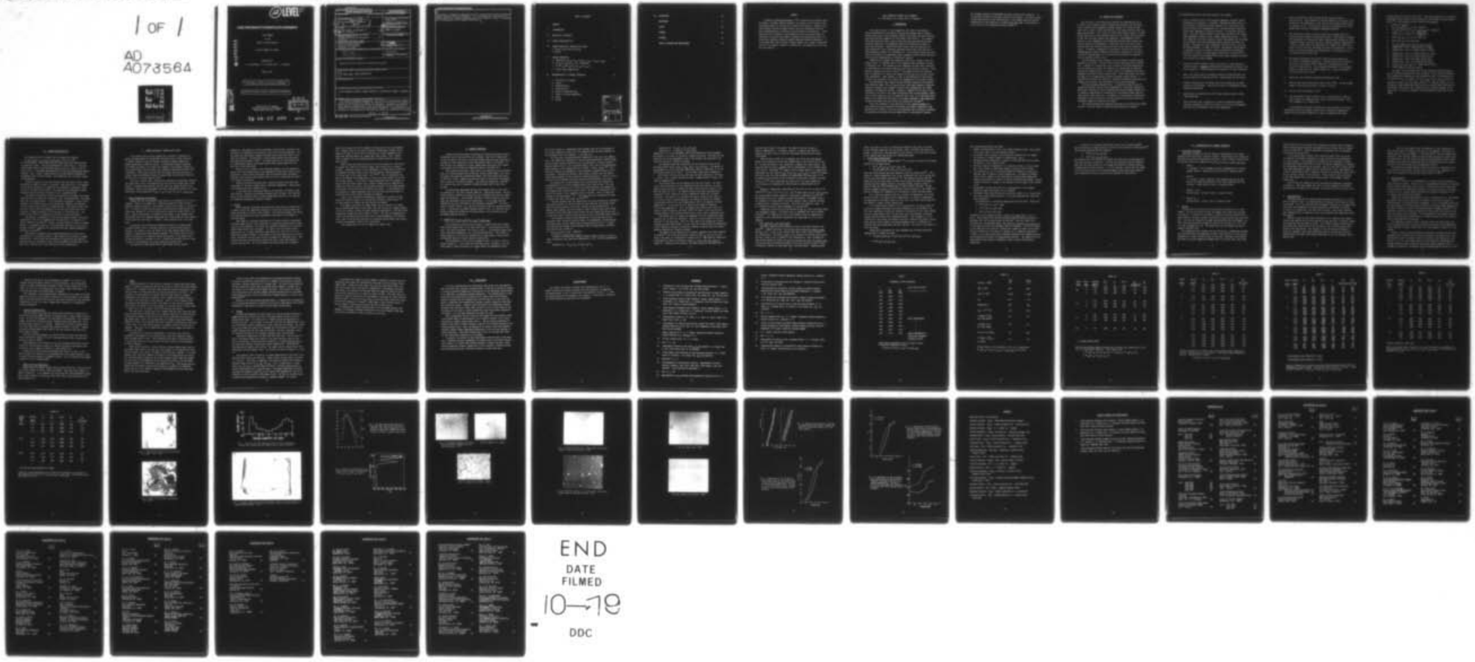

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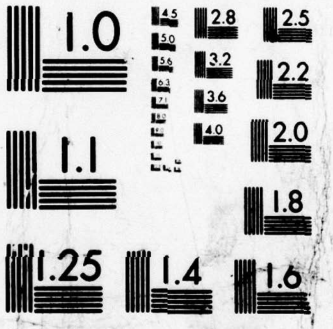

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LEAD ZIRCONATE TITANATE (LZT) CERAMICS

FINAL REPORT
to the
Office of Naval Research

Contract N00014-76-C-0659

Submitted by

J. H. Rosolowski, R. H. Arendt and W. J. Szymaszek

August 1979

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General Electric Company
Corporate Research and Development
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SRD-79-123

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
⑥ LEAD ZIRCONATE Titanate (LZT) CERAMICS.

5. TYPE OF REPORT & PERIOD COVERED
FINAL REPORT
76 May 01 - 79 April 30

6. PERFORMING ORG. REPORT NUMBER
⑭ SRD-79-123

7. AUTHOR(s)
⑩ J.H. Rosolowski, R.H. Arendt,
[redacted] J.W. Szymaszek

8. CONTRACT OR GRANT NUMBER(s)
⑮ N00014-76-C-0659

9. PERFORMING ORGANIZATION NAME AND ADDRESS
General Electric Co.
Corporate Research and Development
P.O. Box 8
Schenectady, New York 12301

406 617

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
Metallurgy Program Office
Arlington, VA 22217

12. REPORT DATE
⑪ Aug[redacted]79

13. NUMBER OF PAGES
45

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
⑫ 59 p.

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

⑨ Final rept. 1 May 76-30 Apr 79,

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

LEAD ZIRCONATE TITANATE, POWDER SYNTHESIS, PIEZOELECTRIC CERAMIC, SINTERING

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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SUMMARY

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LEAD ZIRCONATE TITANATE (LZT) CERAMICS

J.H. Rosolowski, R.H. Arendt and J.W. Szymaszek

I. INTRODUCTION

This report covers a 3 year program of work aimed at developing a better understanding of the factors relating the methods used to prepare, process and sinter a lead zirconate titanate (LZT) powder and the electrical and piezoelectrical properties of the ceramic fired from it. The technological motivation for such a study arises from the great difficulties manufacturers experience in reproducibly making LZT piezoelectric bodies to rigid specifications. These difficulties result from the sensitivity of final properties to the sintering conditions and the fact that each lot of powder generally behaves in a different way. The scientific motivation arose from the possibility of generating useful information about powder characterization and the phenomenology of sintering in general.

Commercial LZT powders are prepared by calcining a mixture of the component oxides, or compounds such as the carbonates that decompose to oxides on heating in air. The formation of the compound LZT under these conditions is controlled by solid state diffusion across inter-particle contacts. Intermediate compounds are known to form.(1) The degree to which the reaction goes to completion in a given time depends on the particle size and calcination temperature. These factors, as well as the perfection of the initial mixing of the reactants, also control the homogeneity of the product powder.

The observation that ceramics having different properties are obtained when different powder lots are processed and fired under nominally identical conditions suggests that incomplete reaction and inhomogeneity are common properties of commercial powders. Evidence in support of this view is also available in the form of the common observation that calcined powders contain up to several weight per cent of unreacted ZrO_2; also, in a controlled experiment, it was found that the density of ceramics depended on the temperature at which the powder from which they were pressed was calcined(2).

Since the attainment of the objectives of the program depended to a great degree on having available LZT powders that behave reproducibly when processed into ceramics, the first task undertaken was to develop a technique for producing such powders having compositions of technological interest.

The technique chosen for development was that of molten salt synthesis. It is described in detail in the next section of this report. The later sections contain descriptions of the characteristics of LZT powder made this way and observations on the properties of ceramics made from them. Two previous reports of work on this program have been issued(3,4).

II. MOLTEN SALT SYSTHESIS

The objective of the molten salt technique for synthesizing LZT is to effect a more complete reaction between the reactants, and to produce a more compositionally homogeneous product powder, by coating the reactants with a liquid in which the reaction to LZT occurs and from which the powder precipitates. This liquid, in which atoms diffuse rapidly, in effect brings large areas of many reactant particles into contact with each other so that they can react rapidly and completely. The homogeneity of the product is still dependent on the perfection with which the reactant powders are mixed but the dependence is much less than in the case of calcination where the reaction takes place only at the contacts between particles. In addition, homogeneity is improved by the fact that the most thermodynamically stable compound forms directly instead of at the end of a series of intermediates, as is the case with calcination of powders of even the smallest particle size.

The development of this technique for LZT synthesis required several problems to be solved. The first was to choose the proper liquid composition. Although it is known that oxide reactions of the kind required can occur in molten ionic salts, the specific salt chosen must be such that the desired compound forms in it either alone or in combination with other compounds which may be easily removed later. After some trials, the choice was made to use an approximately eutectic mixture of NaCl and KCl. A fluoride melt (KF-KCl) was tried but a difficult-to-remove lead fluoride was formed with the excess lead introduced into the reactant mixture.

The other problems addressed were: to develop an effective way of mixing the reactants and the salts homogeneously; to develop a method for efficiently removing the excess unreacted PbO from the product powder; and to develop a rapid method of separating the fine product powder from the water used to remove the salt. In addition, it was desired to develop the technique in such a way that it have the potential for being scaled up to economical commercial production of powder.

The recipe developed for producing LZT powder by the molten salt method follows. It can be scaled to make any desired quantity of product.

The standard batch used in this work yielded 1 kg of powder.

1. First, an aqueous slurry of the reactant compounds, typically oxides, hydroxides and carbonates, is prepared. Although the molten salt solvent provides an enhanced reaction condition, it is not able to completely overcome the inhomogeneities in a reaction mixture containing large, dense aggregates of reactant material. To alleviate this problem, it has been found necessary to pass those reactants which contain these aggregates through a brief, intense comminution process. It has been found that stirring an aqueous slurry of the powders for 60 seconds in a stainless steel food processing blender greatly alleviates this problem. The product of this comminution, usually the TiO_2, ZrO_2 and any desired dopants, is added to the PbO. The quantity of PbO present is generally 2-10 wt.% in excess of that required for stoichiometry. Since PbO is soluble in dilute aqueous acetic acid, the excess PbO in the final product can be removed with an acid wash following the removal of the molten salt water washing.

2. Slurry the reaction mixture in H_2O at the rate of 1 litre H_2O per kg reaction mixture. Vigorous stirring should be employed to obtain a complete suspension. Settled material will generally not react completely.

3. When a well mixed slurry is attained, continue stirring and add 0.454 kg/1 kg reactants of both NaCl and KCl (.908 kg total) as the solids.

4. Continue stirring until the mixture gels due to hydration (or carbonation) of the reactants. This gel will retain its homogeneity during subsequent processing.

5. Remove water by evaporation at 200°C using suitable vessels, Teflon lined being best.

6. React the dried cake in either Pt, Pt lined or stabilized zirconia crucibles (covered) at 1000°C for 30 min to 1 hr in an air atmosphere, then cool at any convenient rate to room temperature.

7. Dissolve the NaCl-KCl from the reacted cake using distilled or deionized water. The solubility of the salt mixture is 0.5 kg per litre of water at room temperature. Glass vessels and a motor driven stirrer are adequate to use. The brick-like cake will disintegrate into a fine powder that contains no perceptibly aggregated material.

8. The supernatant solution will have a high ionic strength which will cause the product powder to flocculate and settle when mixing is stopped. The supernatant can therefore be nearly quantitatively decanted to allow repeated washings with distilled water. Washing should be repeated until a stage is reached where the supernatant will remain milky white after about 10 min of settling, indicating cessation of flocculation. At this point the residual chlorine ion concentration is low enough so as not to interfere with the next step.

9. Add enough concentrated acetic acid to make the slurry about 0.1M (4 litres 1 M CH_3COOH/1 kg product). Continue mixing for 30 to 60 min. The color of the product should lighten due to dissolution of the excess Pb added initially. Add an anionic flocculant (0.1 w/o aqueous solution of Hercafloc 821, Dupont Chemical Co.), allow the powder to settle and decant the liquid.

10. Repeat the acid treatment-flocculation-decantation twice.

11. Wash two more times during dilute acetic acid (10^{-3}M). Use the minimum amount of flocculant necessary in steps 9, 10 and 11.

12. Dry the slurry by heating at 150°C.

13. The dried powder should be heated in air to about 500°C for about 20 min to remove any remaining water, acetic acid and flocculant. After this treatment it is ready to use.

A new method of producing LZT powder will only be useful if it allows introduction of all the elements usually used to modify LZT compositions. Powders of the following composition or range of composition have been prepared during the course of this work. (The charge imbalance in the formulas containing Cr and U reflects the uncertainty in the valence of those elements in LZT.(5)) The reactants used are listed in the Appendix.

1. $Pb(Zr_{.52}\ Ti_{.48})\ 0_3$;
2. $Pb_{.95}\ Sr_{.05}(Zr_xTi_{1-x})\ 0_3$ for $.52 \le X \le .56$;
3. $Pb_{.94}\ Sr_{.06}(Zr_xTi_{1-x})_{.997}\ Fe_{.003}0_{2.9985}$ for $.40 \le X \le .60$;
4. $Pb(Zr_yTi_{1-y})_{1-x}\ Cr_x0_3$ for $\begin{Bmatrix} .02 \le X \le .04\ ; \\ .52 \le y \le .54 \end{Bmatrix}$
5. $Pb(Zr_{.52}Ti_{.48})_{1-x}\ U_x\ 0_3$ for $.02 \le X \le\ .03$;
6. $Pb(Zr_{.52}Ti_{.48})_{.97}\ Fe_{.01}Cr_{.02}0_3$;
7. $Pb_{.994}Ca_{.003}Mg_{.003}(Zr_{.52}Ti_{.48})_{.97}Fe_{.01}Cr_{.02}0_3$;
8. Compositions 2 with 1 weight percent of Nb_20_5;
9. Compositions 2 with 1.1 weight percent of Sb_20_3;
10. Compositions 2 with 0.75 weight percent of As_20_3;
11. Compositions 2 with 1.76 weight percent Bi_20_3;
12. Compositions 2 with 0.68 weight percent V_20_5;
13. Compositions 2 with 1.66 weight percent Ta_20_5;
14. $Pb_{.95}Sr_{.05}(Zr_{.54}Ti_{.46})0_3$ + 1 weight percent La_20_3;
15. $Pb(Ni_{.333}Nb_{.667})_{.54}Zr_{.135}Ti_{.325}0_3$.

The above list illustrates that all the important modifying elements can be introduced during molten salt synthesis. So far, with one exception every composition attempted has been successfully made. The exception was the composition $Pb_{.94}\ Ca_{.05}Mg_{.01}\ (Zr_{.52}Ti_{.48})_{.97}\ Fe_{.01}Cr_{.02}0_{2.985}$ which was reported to produce very slow aging ceramics.(6) Chemical analysis of the synthesized powder showed much lower levels of Ca and Mg than those given in the formula, indicating a lower solubility limit of those elements in LZT. Composition 7 in the list represents the more probable composition of that powder.

III. POWDER CHARACTERISTICS

The characteristics of powders from the composition sequence

$Pb_{.94}Sr_{.06}(Zr_x\ Ti_{1-x})_{.997}\ Fe_{.003}O_{2.9985}$; $0.40 \leq x \leq 0.60$

will be described. These powders are all light yellow and darken readily on exposure to light. They are agglomerated as seen in Fig. 1. The individual powder grains are rounded and range in size up to about 0.7 µm as seen in Fig. 2. The powder agglomerates are friable and disintegrate during pressing. Fig. 3 shows a typical particle size distribution obtained by measurement with a Coulter Counter. The "particles" are, of course, almost all agglomerates.

Chemical analysis for Na and K revealed that the powders contain about 680 ppm Na and about 170 ppm K in solution. These values are to be compared to the figures obtained on a commercial LZT produced by calcination, which were about 115 ppm Na and 30 ppm K. The analyses were performed by atomic absorption after dissolving the powder in hot, concentrated HCl.

The amount of unreacted zirconia was determined by weighing the residue remaining after the powder was dissolved in hot, concentrated HCl. The amount found was 0.02 weight percent. If the procedure of whipping a slurry of the reactants in a blender (step 1 of the recipe) were skipped, the unreacted zirconia content rose to about 0.4 weight percent. This result clearly indicates that large, hard ZrO_2 aggregates in the reaction mixture have to be broken up if complete reaction is to take place in the molten salt. The break up could also be accomplished by milling the reaction mixture.

The presence of aggregates in the reaction mixture should be even more troublesome in the case of powders made by calcination. An analysis of a "good" commercial LZT powder(7) showed a zirconia content of about 1.3 weight percent. In commercial practice it has been found that such a level of unreacted zirconia is generally not associated with poor sintering behavior or difficulty in poling(8).

The results of examining the as-produced powders with X-rays can be illustrated by the following results. When samples from 3 batches of powder having Zr/Ti = .53/.47 which were synthesized in essentially the same way were analyzed, the tetragonal a and c lattice parameters obtained were 0.404 and 0.411, 0.405 and 0.413, and 0.406 and 0.414 nm, respectively.

IV. POWDER PROCESSING, PRESSING AND FIRING

The essential basis of this program was to develop a technique for making starting powders of reproducible characteristics so that variations in ceramic properties could be reliably ascribed to powder composition, powder processing or method of firing. In developing standard techniques for forming the powder into ceramic test samples it was assumed, subject to later verification, that the molten salt synthesis technique did fulfill this requirement. Verification would be done by showing that the properties of ceramics made from different batches of powder made, processed and fired the same way lie in a narrow range of values.

The basic criteria used to develop the techniques of processing, pressing and firing used in this investigation were that the fired ceramic have a high density, a uniform microstructure, and that lead loss during firing be well controlled. Most of this development was done using powders having Zr/Ti ratios around that of the composition $Pb_{.94} Sr_{.06} (Zr_{.53}Ti_{.47})_{.997} Fe_{.003}O_{2.9985}$.

A. Powder Processing and Pressing

Samples for this investigation were pressed in a Carboloy die of 2.54 cm diameter. About 5 g of powder was loaded and pressed at 69 MPa (10 Kpsi) holding 1 minute at pressure. This yielded a green body of about 2.5 mm thickness. In order to insure uniform density, these discs were then placed in a rubber bag, immersed in oil, and isostatically pressed at around 340 MP a (50 Kpsi). When as-made powder was pressed in this manner it was observed that the pressed discs were somewhat fragile and that, even though the final density of the fired discs was high ($< 7.6\ Mg/m^3$), they contained a few, very large pores.

Accordingly, the procedure was adopted to process the as-made powder by adding stearic acid as a pressing lubricant to achieve better particle packing. Two weight per cent was chosen as the near minimum amount that resulted in a green body having adequate strength. The stearic acid was introduced by dissolving it in benzene, adding the solution to the powder, then milling the mixture to disperse it well. Milling was routinely done for about 24 hours in a polyethylene jar using stabilized zirconia balls.

The mixture was then poured into an open beaker and the benzene evaporated. The powder was stirred constantly during drying to prevent stratification or segregation of the stearic acid as the solvent evaporated. The dry powder was then passed through a 60 mesh nylon screen after which it was ready for pressing. The densities of green bodies pressed from such powder were found to be around 5.7 Mg/m^3. The final densities of fired bodies were not significantly greater than those pressed from as-made powder but they were free of the large pores.

Stearic acid was chosen as the lubricant because it can be completely burned out of the pressed body at low temperature before final firing at high temperature. Water soluble lubricants such as polyvinylalcohol and methyl cellulose leave residues after burnout that are rich in sodium and were therefore avoided in this work.

Besides the method described above, freeze drying has also been used successfully to produce a powder with no lubricant segregation. Spray drying would probably also work satisfactorily.

It was found that a high green density was necessary to achieve a high final density, therefore the pressing pressure had to be high. The isostatic pressing step routinely used to insure uniform green density is not required for producing satisfactory technical ceramics.

B. Firing

After pressing, the binder was burned out of the disks by laying them on a powder of their own composition spread on a stabilized zirconia plaque and firing uncovered in air for 1 hour at 600°C. The fractional weight loss during this step was always within the experimental uncertainty of the amount of lubricant added.

Lead oxide is a volatile constituent of LZT whose content in the powder and final ceramic must be well controlled if reproducible piezoelectrical proprties are to be obtained. The molten salt systehsis technique, by its nature, affords good control over the powder. To control lead loss during firing, pressed discs of a single composition were placed in a stack of 5 to 6 in a stabilized zirconia crucible. Loose powder of the same composition was placed under, around and over the stack as well as between the individual discs. The crucible was then covered with an alumina disc with a small gap between it and the crucible top. All of the alumina and zirconia ware was "seasoned" before first being used to fire samples by being used to fire loose powder only. Samples fired in this manner typically experienced a weight loss of around 0.3%, part of which can be attributed to a slight chipping of the edges when adhering powder was scraped away after firing. Fig. 4 shows a stack of samples and the surrounding powder as removed from the crucible after firing.

Some firings were made with the stack of discs placed on a bed of powder spread on a stabilized zirconia plaque, then covered with a zirconia crucible. Additional control of the atmosphere of volatile PbO was effected by sometimes including "donor blocks" made of pressed, unreacted powders of PbO and ZrO_2 in the weight ratio 2.3/1.(10,11) This is essentially the same as the method used commercially to control the lead content of LZT ceramics during firing. It was found in these experiments that the presence of donor blocks did reduce weight loss, indeed a weight gain was sometimes observed, but there was always a top-to-bottom variation in the weight changes of the discs in the stack with and without the blocks. It was therefore in the interests of sample uniformity that the previously described method of firing the discs while buried in powder was adopted.

Since it was learned that developing a technique to analyze LZT for lead to an accuracy around ± 0.1 percent would require a major effort (12). No lead analyses of ceramics was made during the program.

The samples were fired in oxygen rather than air because it is known, and was demonstrated again in this work, that that results in a higher density. It does not, however, affect the other properties appreciably. The peak firing temperatures ranged from about 1250°C to 1325°C. The time at temperature was 1 hour with the heat-up and cool-down rates varying depending on the furnace used. Most of the firings were done in a platinum winding heated tube furnace in which the atmosphere could be well controlled.

The average grain size of all samples was around 3.5μm.

V. CERAMIC PROPERTIES

Besides having the purpose of showing that modifying elements could be introduced into LZT during molten salt synthesis, many of the compositions in the list given in Section II were made because some data were available on ceramics of those compositions fired from powders made by calcination. In what follows, the properties of some ceramics made from molten salt synthesized powder will be given and comparisons made to available data.

After sintering the discs, their density was measured by water displacement, the surfaces ground flat on 600 grit silicon carbide paper, and silver electrodes were applied by painting on Dupont 7713 silver paste and firing at 600°C for 1 hour. Samples were poled at 120°C in Fluorinert (3M Company) with a field of 2.36 MV/m (60 V/mil). The field was applied for 3 periods of 5 minutes each with a reversal of direction after each of the first 2 periods.

The pre-poling capacitance and the loss tangent (Tan Δ) of the discs was measured at 1 KH_z with a General Radio Co. Capacitance Bridge. The prepoling relative dielectric constant (K_o) was determined from the disc capacitance and dimensions. After poling, the free, relative dielectric constant (K_{33}^T) was determined from the disc capacitance, and the planar coupling coefficient (k_p) was determined by the resonance technique(13). The piezoelectric strain constant, d_{31}, was also calculated from the resonance measurements. A Berlincourt d_{33} Meter (Channel Products, Inc.) was obtained about mid-way through the program and the piezoelectric strain constant d_{33} was afterwards measured directly.

A. COMPOSITION $Pb_{.94}Sr_{.06}(Zr_xTi_{1-x})_{.997}Fe_{.003}O_{2.9985}$

X-ray diffraction patterns were obtained on samples taken from ceramic discs having compositions of the above type with x's lying between 0.40 and 0.60. The lattice parameters are given in Table I. The patterns showed sharp lines indicating homogeneous, well crystallized materials. This stands in marked contrast to the results obtained with as-made powders, which showed a considerable degree of crystal disorder (Section III).

The progressions of the lattice parameters with x in Table I show an abrupt change at x = .530, where the heretofore purely tetragonal x-ray patterns begin to show the presence of a minor amount of rhombohedral phase.

The relative amount of rhombohedral phase present could not be determined in any of the compositions shown, but it is apparent that the phase boundary of the tetragonal field lies between x = .520 and .530.

The electrical and piezoelectrical properties of LZT vary with composition. The composition dependence of the post-poling dielectric constant (K_{33}^{T}) and the planar coupling coefficient (k_p) is particularly strong, with both peaking sharply close to the tetragonal ($PbTiO_3$ rich) side of the morphotropic phase boundary at room temperature in the $PbTiO_3$ - $PbZrO_3$ system.(14) Fig. 5 shows the composition dependence of these properties obtained during this investigation. Reasoning by analogy, these results indicate that the morphotropic phase boundary in this Sr and Fe containing material is close to x=0.53, and thus little different from that found when these modifiers are absent.

The properties of three samples from a batch having the composition corresponding to x=0.53 were measured about 3 days after poling. This composition is characteristic of a "hard" LZT whose properties are expected to lie between those of Military Standard Type I and Type III (Vernitron's PZT-4 and PZT-8) because of the relatively small Fe content. Table II shows the average of the measurements (15). (the aging rates were measured over about 40 days) along with values given for PZT-4(16).

The data indicate that the samples were very good piezoelectric ceramics. Particularly notable are the low losses at both high and low driving fields, high Q and small change in dielectric constant at high driving field. In general these samples, whose Fe content is about one-half that usually added to reduce losses under high driving fields, have the higher K_{33}^{T} and d_{33} associated with a Type I ceramic along with the low Tan Δ associated with a Type III.

Five samples having the same composition as discussed above except containing twice as much Fe were also made. No measurements at high driving field were made, and the samples had an average density close to 7.7 Mg/m^3, but otherwise the average values obtained were not significantly different from those given in Table II.

B. $Pb_{.95}Sr_{.05}(Zr_xTi_{1-x})O_3$ + additives

A number of elements that commonly exhibit valence states of +3 and +5 were incorporated into three base compositions of LZT. The base compositions were:

Composition A; $Pb_{.95}Sr_{.05}(Zr_{.52}Ti_{.48})O_3$, Composition B; $Pb_{.95}Sr_{.05}(Zr_{.54}Ti_{.46})O_3$,

Composition C; $Pb_{.95}Sr_{.05}(Zr_{.56}Ti_{.44})O_3$.

Composition A is on the tetragonal side of the morphotropic phase boundary and exhibits an increase in dielectric constant on poling. The other two compositions are on the rhombohedral side of the boundary and experience a decrease in dielectric constant on poling.

The elements added were introduced into the reaction mixture as the following oxides; Nb_2O_5, Sb_2O_3, Ta_2O_5, Bi_2O_3, V_2O_5 and As_2O_3. The amount of Nb_2O_5 added was 1 w/o of the base composition, which is equivalent to 2.4 a/o substitution of Nb for Zr and Ti. All the other oxides were introduced in quantities which, for the cations, were atom-for-atom identical to the Nb_2O_5 additions. Also, a powder was made in which 1 weight percent of La_2O_3 was added to Composition B.

The ceramics made from the powders fell into two classes. The first class, which included all of the compositions made with added Bi, As and V, quickly arced over when an attempt was made to pole them at a field of 2.36 MV/m (60 V/mil) at 120°C. The highest poling field these specimens could withstand at 120°C (which was the only temperature tried) was 1.18 MV/m *(30 V/mil). The values of* k_p *achieved were small, typically less than 0.1.* In the case of the As and Bi additions, the change in dielectric constant on poling was positive for base Compositions A and B, and negative for base Composition C. In the case of the V addition the change was negative for all base compositions. Also, the samples with added As and V had to be fired at 1250°C because at the usual 1325°C the stack of discs and the surrounding powder in the crucible sintered into a hard, nearly inseparable mass.

The second class of ceramics was composed of all the compositions made using Nb, Sb, La and Ta as additives. These all could be poled at 2.36 Mv/m and 120°C in the usual way. Table III lists some of the properties of these ceramics one hour after poling. In all cases the ceramics based on Compositions A and B showed an increase in dielectric constant on poling while the ceramics based on Composition C showed a decrease.

The results for Nb addition are in general agreement with those obtained by Kulcsar(17) who found the greatest increase in K_{33}^T, k_p and d_{31} to occur when it was added to a Composition B without the Sr. When added to Composition B and poled at 4 MV/m, he achieved a higher k_p (0.56) than that shown in Table III. Taking that into account, the other quantities had magnitudes in line with those shown in the table. The same is true for Ta and La added to Composition B. In general, however, it appears that Kulcsar's ceramics were about twice as lossy as those made from molten salt synthesized powder.

From the data in Table III is apparent that Sb has the same general effect on the properties of the base compositions as do the additives Nb and Ta. No data were found in the literature to compare with these results. Nor could any data be found to compare with the observations on the ceramics doped with V and As. Haertling (18) reports on hot pressed samples of a composition containing 2 a/o Bi, namely $Pb_{.99}(Zr_{.53}Ti_{.47})_{.98}Bi_{.02}O_3$, in which he assumed that the Bi went into the structure as a pentavalent ion replacing Zr or Ti. He reports k_p's of around 0.6 and a decrease in dielectric constant on poling Atkin et al (19) have shown that Bi enters LZT of this base composition as a trivalent ion replacing Pb, while Nb goes in pentavalently for Zr or Ti.

Samples of compositions containing Nb, Sb and Ta as well as some of the composition $Pb_{.94}Sr_{.06}(Zr_{.53}Ti_{.47})_{.997}Fe_{.003}O_{2.9985}$ with and without excess ZrO_2 were tested for their response to hydrostatic compression cycling.(20) The pressure cycle was a stepwise increase from ambient to 68.98MPa (10^4psi) in 4 minutes, a 5 minute hold at the peak pressure, then a stepwise decrease to ambient with a 2 minute hold there. The cycle was repeated 5 times. It was intended to simulate deep submergence of sonar devices.

Comparison of pre and post-cycling data on K_{33}^T, k_p, Tan Δ and aging showed only negligible changes. The results were in agreement with those obtained by Palmer(21) who subjected 15 LZT's that differed either in composition or supplier to cyclic hydrostatic compression and found them all to be little affected.

C. $Pb(Ni_{.333}Nb_{.667})_{.54}Zr_{.135}Ti_{.325}O_3$

The above composition was reported to have a very high dielectric constant(22). Samples were made, and six days after poling the average values for K_{33}^T, Tan Δ, k_p and d_{33} were found to be 4470, 0.010, 0.418 and $434X10^{-12}$ C/N, respectively. The values given in the reference for one day after poling are 6727, 0.028, 0.570 and $700X10^{-12}$ C/N, respectively. Thus, although the same poling temperature (35°C) and field (2.5 Mv/m) were used, the samples made from the molten salt synthesized powder did not pole as well or have as high a dielectric constant as those made from a calcined powder. Comparing aging rates, the values -2.5 and -1.6 percent per decade for K_{33}^{T} and k_p are given in the reference (measured over one decade), while +0.63 and 0.00 percent per decade , respectively, were measured over the period 6 to 170 days after poling on the samples made from molten salt synthesized powder.

D. Slowly Aging Compositions

In the Second Annual Summary Report (4) an account was given of the aging behavior of two compositions;

1. $Pb(Zr_{.52}Ti_{.48})_{.97}Fe_{.01}Cr_{.02}O_3$ and
2. $Pb_{.94}Ca_{.05}Mg_{.01}(Zr_{.52}Ti_{.48})_{.97}Fe_{.01}Cr_{.02}O_3$.

These were made because they were reported to have low aging rates(6). (The second is a batch composition since it was established that the Ca and Mg solubilities were much smaller than shown.(3)) The behavior seen was that the aging rate was low until about 120 days after poling when both the dielectric constant and loss tangent started to increase rapidly, reached a peak in about 100 days and then decreased again in about another 100 days. No significant changes in d_{33} or k_p occurred while this was going on. The report was written as K_{33}^{T} and Tan Δ appeared to be decreasing to their starting values.

Fig. 6 shows the aging of K_{33}^{T} for a ceramic of Composition 1 as of the present writing. The aging curve of Composition 2 is similar in appearance. The magnitudes of the peaks relative to the value a few days after poling vary from sample to sample in both compositions.

In the Second Annual Report it was speculated that the effect might be caused by a change occurring in the grain boundaries of the specimens, and that this hypothetical change was related to the presence of Cr, since nothing like this aging behavior has ever been seen in any non-chromium containing ceramic made from molten salt synthesized powder. This hypothesis is less attractive at the present time because the cyclic change of K_{33}^{T} shown in Fig.6 would require cyclic change in the grain boundary, and it is difficult to envision what the driving force for that could be. The cause of the effect is still not known.

During the investigation of this phenomenon the following additional compositions of ceramic were made:

3. $Pb_{.994}Ca_{.003}Mg_{.003}(Zr_{.52}Ti_{.48})_{.97}Fe_{.01}Cr_{.02}O_{2.9985}$,

4. $Pb(Zr_{.52}Ti_{.48})_{.98}Cr_{.02}O_3$.

The following observations were made:

a. Samples of Compositions 3 and 4 also showed anomalous aging. The presence of Cr, then, seems to be the important factor.

b. The sudden, rapid increase in the dielectric constant and loss tangent was observed in unpoled samples of Compositions 1 and 4.

c. Storage of poled, Composition 4 samples at 125°C and 225°C did not cause the effect to occur within 30 days.

d. Storing a sample of Composition 4 in vacuum for 2 hours or in wet steam for 1 hour caused no significant change in the K_{33}^{T} or Tan Δ values.

e. The electrodes on all Cr containing samples were found to be much less adherent than on samples of other compositions. On samples of Compositions 1 and 2, removal of the electrodes by scraping and grinding and reapplying electrodes of either air drying silver paste or indium - gallium eutectic resulted in changes in the measured values of K_{33}^{T} or Tan Δ within $\pm$ 10%.

f. Micrographs revealed that there was no open porosity in the samples. Densities ranged from around 7.6 to 7.8 Mg/m^3.

g. Microprobe scans revealed some areas that were richer in Cr. These looked like small second phase particles. No Cr over background was found near grain boundaries.

Some additional Cr containing compositions were also made. These were:

5. $Pb(Zr_{.53}Ti_{.47})_{.98}Cr_{.02}O_3$,
6. $Pb(Zr_{.53}Ti_{.47})_{.96}Cr_{.04}O_3$,
7. $Pb(Zr_{.54}Ti_{.46})_{.96}Cr_{.04}O_3$.

The density of all samples was high, lying in the range from 7.7 to 7.9 Mg/m^3. These samples had fired-on electrodes applied and their dielectric constants were in the range between 650 and 850. They were stored for a few weeks and, when measured again, the dielectric constants were found to be in the range of 10,000 with extremely high loss tangents. With those samples it was found that the dielectric constant was reduced to nearly the original value by storing for a few days in a vacuum, or at a moderate temperature (100°C), or by removing the poorly adhering electrodes and reappling contacts of air-drying silver paste or indium-gallium eutectic. The samples were not poled because they tended to experience current run-away and dielectric break down.

In order to see if some of the effects seen in the Cr bearing samples were also present in samples bearing U, which is also reported to reduce aging(23), the following compositions were prepared:

8. $Pb(Zr_{.52}Ti_{.48})_{.97}U_{.03}O_3$.

9. $Pb(Zr_{.52}Ti_{.48})_{.98}U_{.02}O_3$.

The ceramics had a low density (∿7.2 Mg/m^3) and could not be poled because of their low electrical resistance. The fired-on electrodes were well adhering, and there was some increase in loss tangent and dielectric constant during a storage period of about 200 days. It is not, however, certain that the change is of the type seen in the Cr containing samples rather than being caused by more conventional effects arising from the presence of open porosity.

VI. REPRODUCIBILITY OF CERAMIC PROPERTIES

A. Decription of Powders

Experiments designed to show the degree of reproducibility of ceramic properties were made using 7 batches of powder. These batches were synthesized, processed and pressed as described in Sections II and IV except as noted below. All batches were of the composition $Pb_{.94}Sn_{.06}(Zr_{.53}Ti_{.47})_{.997}Fe_{.003}O_{2.9985}$.

1. Batch A

   A 2 kg batch. Use of blender to break up agglomerates in reactant powders omitted. Powder milled for 24 hours to disperse binder.

2. Batch B

   A 1 kg batch. Small, stainless steel blender used only for this batch, and slight discoloration of the slurry indicated that wear occurred. Powder milled 24 hours to disperse binder.

3. Batches C, D, E

   One kg batches. Milled 24 hours to disperse binder.

4. Batches F, G

   One kg batches. Milled 1 hour to disperse binder.

B. Firing

Pressed discs were fired in a Glo-Bar heated box furnace or in a tube furnace. For the box furnace firing, the samples were loaded into crucibles (one batch to a crucible) as described in Section IV and the crucibles then placed inside a covered, seasoned, stabilized zirconia box that had a gas inlet port. This box was flushed with oxygen and then placed into the furnace. An oxygen flow was maintained through the zirconia box at about 9.3×10^{-3} m^3/h (0.1 cfh) throughout the run. The oxygen flow into the furnace was kept at around 0.28 m^3/h(3 cfh).

The temperature-time schedule for this firing was; a temperature increase rate of 85°C/h from room temperature to 850°C, then 130°C/h up to the firing temperature of 1325°C, which was held for one hour. The power to the furnace was then cut and the temperature dropped 330°C in the first hour, then 130°C, 100°C and 80°C in the next three hours respectively and more slowly thereafter. The box containing the crucibles was removed from the furnace when its temperature was around 200°C. Furnace temperature was measured with a thermocouple placed near the zirconia box.

In the second type of firing, discs from each powder batch were placed in crucibles as previously described, but each crucible was fired separately in a tube furnace. After flushing, the oxygen flow rate through the furnace was maintained around 0.028 m^3/h (0.3 cfh). The furnace temperature, as measured by thermocouples located near the crucible, went up at the rate of about 200°C/h from room temperature to 1260°C, where it was held for 1 hour, then reduced at a rate of about 200°C/h down to where the controller was turned off (about 200°C) and the furnace allowed to cool naturally. Firing could be done more rapidly in the tube furnace than in the box furnace because of the former's smaller thermal mass.

After firing, the sample discs were electroded and measured as described in Section V. Data from samples that were in any way damaged or that showed strong multiple resonances were rejected. The results are shown in Table IV and V.

C. Reproducibility

Considering the data on ceramics made of powder from Batches B, C, D and E given in Tables IV and V, the reproducibility of density for each type of firing is excellent. Also, the variation of the averages of K_{33}^T and k_p for samples from each batch, when compared to the grand averages for all batches, are within ± 4% and ± 7%, respectively, for each type of firing. These values represent good reproducibility as compared to what can be expected from commercially available powders.

However, except for those made from Batch E, it is apparent that samples from the same powder batch did not achieve the same absolute, or relative, degree of poling after the two kinds of firing. For instance, samples from Batches B and D poled well after firing in the box furnace, but relatively poorly after firing in the tube furnace. The converse is true for samples from Batch C. There are, therefore, still some differences between the nominally identical powder batches that makes them respond differently to the two different firing methods used.

There is some evidence that the difference in peak temperature between the two types of firings is the cause of the difference in behavior of samples made from the same powder. It was observed(24) that when samples made from Batch C were fired at 1320°C but with the same heating and cooling rates as experienced in the tube furnace firings (firing temperature 1260°C), their properties were similar to those shown for the samples made from that powder and fired in the box furnace (firing temperature 1325°C).

The samples from powder Batches F and G were much less reproducible than those from the other batches, and they had low values of k_p, apparently as a result of shortening the milling time from 24 hours to 1 hour.

D. Microstructure

Figures 7a, 7b and 7c are micrographs of a ceramic specimen from Batch C fired in the box furnace. Figure 7a is a low magnification picture of a polished surface showing large pores in the ceramic. The presence of such large pores, which account for the significant fraction of the total porosity of the piece, is typical of all ceramics made from molten salt synthesized powders as well as ceramics made from calcined powders.

Figure 7b is a higher magnification view of a polished section. The rounded precipitate particles are ZrO_2 which is present to the extent of about 0.4 volume percent, as determined from a micrograph. This is considerably more than the approximately 0.03 volume percent present in an as-made powder prepared with the step of passing a slurry of the reactant powders through a blender(3) The additional zirconia was picked up from wear of the zirconia balls used to disperse the stearic acid by milling. It was determined by wet chemical analysis that the milling step introduced about 0.5 weight percent ZrO_2 into a batch of powder being processed for pressing.

For comparison, Figure 8 shows a polished section of ceramic made from Batch A powder milled for 24 hours for which the omission of the blending step in the synthesis procedure should result in a ZrO_2 content of about 1% in the ceramic.

Figure 7c shows the grain boundaries revealed on a polished section after treatment with a boiling, 5% HCl solution containing a few drops of HF. The average grain sizes of ceramics from all 5 batches in this firing lie in the range 3.7 ± 0.2 μm. The average grain size was obtained by determining the average distance between successive points where grain boundaries cross a straight line drawn on a micrograph, and then multiplying the result by 1.5(25).

Figures 9a, 9b and 9c are the analogues of Figures 7a, 7b and 7c for ceramics fired from Batch C powder in the tube furnace. The average grain sizes of ceramics from Batches B through E fired in that furnace lie in the range 2.6 $\pm$ 0.2 μm. The average grain size of the ceramic from Batch A is 1.6 μm but the grain size distribution is bimodal.

The difference in the average density obtained in the two types of firings appears to be due to the presence of some air in the box furnace, since experiments in the tube furnace with fast and slow rates of heating to the sintering temperature (6.5 and 12.5 hours, respectively) resulted in no significant density differences.

E. Effect Of Unreacted ZrO_2

The low values of k_p shown for ceramics made from Batch A powder led to speculation that the higher content of unreacted ZrO_2 in these samples was the cause. To test this hypothesis, two new powders were prepared. One was Batch E powder, milled for 24 hours and with 1 weight percent ZrO_2 added for a total estimated ZrO_2 content of 1.5 percent. Another was the Batch E powder milled for 1 hour which had an estimated ZrO_2 content of about 0.1 percent. Samples pressed from these powders were fired in the tube furnace in the same way as those shown in Table V.

The data from these samples are shown in Table VI along with those from Batch A and Batch E samples (1 and 0.5 estimated percent ZrO_2, respectively) previously given in Table V.

There appears to be an increase in k_p with decreasing unreacted zirconia content but the deleterious effect of a shorter milling time previously seen with Batch F and G samples in Table V is also evident here.

Another factor that could be affecting these results is that, in the Batch A powder, the omission of the blending step in the powder synthesis leads to excess zirconia because of incomplete raction. This is different from adding zirconia to a fully reacted powder.

F. Effect Of Firing Temperature

Samples made from Batch E powder which had been milled for 1 hour were fired in the tube furnace at 1200°C, 1260°C and 1305°C. Data from these samples is shown in Table VII. It is apparent that increasing the firing temperature causes only a small increase in the low k_p value that results from milling for only 1 hour instead of 24.

G. Aging

The aging behavior of the dielectric constant of samples made from powder Batch C is shown in Figures 10a and 10b for firing in the box and tube furnaces, respectively. Straight lines were drawn between successive data points, which are not shown, but whose positions in time are indicated by asterisks. The similarity in aging behavior of samples from the same firing is apparent. Furthermore, the similarity extends as well to samples from powder Batches A, B, D and E that were fired in the same way. That is, for all samples fired the same way and regardless of batch, the points in time (on the logarithmic scale) where the slopes of the lines change are closely similar to those shown in Figure 10, as are the slopes of the lines between those points.

The curves of k_p versus log (t) for samples from the same firing and made from the same batch of powder show only a general similarity to each other, and no distinctive change in the curves occurs at the times when the curves for K_{33}^T change slope. Also, the k_p aging curves for samples made from different powders but fired in the same way show only a general, nondistinctive similarity to each other. No curve feature peculiar to samples fired in the same way is apparent. There was also no significant change in loss tangent with time observed in any sample.

Incidentally, all property measurements on LZT discs were routinely preceded by measurements on two standard discs, made from commercial powder, which had been poled in 1974. These standards have shown a random variation of k_p and K_{33}^T within $\pm 1\%$ over the period of time covered by the measurements now being discussed.

These results indicate a strong similarity between samples made from the same powder when fired in the same way, with respect to the operation of those specific factors that control the aging of the dielectric constant. It is also apparent that, for these samples, the details of the aging process for dielectric constant depend strongly on the firing schedule used to make the ceramic, but very little on the magnitude of the dielectric constant or on the degree of poling achieved (as indicated by the magnitude of k_p). The results also indicate that the factors controlling the aging of k_p operate in a generally similar way in all the samples, regardless of the powder batch they were made from or how they were fired.

Poling is the process of preferentially orienting ferroelectric domains in the LZT crystallites, which results in a change in the dielectric constant and planar coupling coefficient of a ceramic body. The post-poling relaxation of those properties toward their pre-poling values (aging) is thought due to the process of re-randomizing the domain structure. This process is thought to be influenced by the specific domain structure obtained and its associated inter-domain stresses, and on the build-up of trapped charge at, or near, grain boundaries(26).

Because of the observations described above, it appears that the magnitude of the post-poling dielectric constant of LZT and its time behavior are strongly influenced by some factor or factors besides domain reorientation.

H. Poling

A poling investigation was made using one of the discs made from Batch E powder milled for 24 hours and fired in the tube furnace as part of the reproducibility study. Its density was 7.77 Mg/m^3 and pre-poling dielectric constant was 1042. In the course of the work, this disc was depolarized 5 times by slow heating to 625°C, holding for 1 hour, and then slow cooling. The value of d_{33} was always zero after this treatment but the successive dielectric constants obtained were 839, 900, 906, 918 and 928. The disc, therefore, could not have been restored to its original condition after each depoling.

Poling bath temperatures of 120°C and 140°C were used. For the tests at 120°C, the depoled sample was repoled in the same direction along the disc axis at successively increasing field strength by 3, 5 minute applications of the field with reversal of direction between applications. The properties were measured 20 minutes after poling. The sample was not depoled until after being poled with the highest field. The results are shown in Figures 11, 12 and 13.

The poling at 140°C was done by 15 minute applications of the field in one direction only (always the same one). These results are also shown in Figures 11, 12 and 13. They show, as expected, that poling at higher field strengths produces higher values of k_p, K_{33}^T and d_{33}. Also, at high fields, a larger value of k_p and d_{33} is achieved when the field is reversed during poling instead of being maintained in one direction. The higher temperature of poling increased the change in k_p and K_{33}^T at the lower field strengths but was not as effective as field reversal at the higher fields. For K_{33}^T, on the other hand, a higher poling temperature resulted in a greater change at all fields.

In neither case, however, did the change in dielectric constant from the pre-poling value equal that obtained one hour after the first poling of this sample (281). Neither did the values of k_p and d_{33} reach those first, one hour values which were 0.539 and 279, respectively. Furthermore, some data (not shown in the figures) was obtained from this sample by poling at 120°C with no field reversal up to a field of around 1.6 MV/m. This data shows the dielectric constant starting at 906 and generally following the curve shown for poling at 140°C. The data for d_{33} and k_p on the other hand, follow the curves for the 120°C poling up to around 1.2 MV/m where a rapid increase occurs so that at around 1.4 MV/m the data follow the 140°C poling curves.

The poling study results therefore show, as do the aging results, that changes in the degree of domain orientation do not cause changes in K_{33}^T that are strictly correlated to those occurring in k_p and d_{33}.

VII. CONCLUSIONS

It can be concluded from the observations made during this investigation that the molten salt synthesis technique offers a good way of making LZT powders of closely controlled composition including all of the modifying elements known to be important in producing desirable properties. The reproducibility of the electrical and piezoelectrical properties of ceramics made from different batches of powder that are prepared and fired the same way is very good compared to experience with commercially available powders prepared by calcining the constituent oxides. Ceramics fired from molten salt synthesized powders generally have dielectric losses about one half or less of those given in the literature for the same or similar compositions made from powders prepared by calcination. All the other properties are about the same.

This investigation did not yield any new insight into the question of how an LZT powder might be characterized so as to predict whether or not a good piezoelectric ceramic could be made from it. The post-poling properties of ceramics were found to depend strongly on details of the powder preparation and firing procedure used. Also, the properties of ceramics made from nominally identical powders showed significant differences in the way they depended on firing conditions. From these observations it must be concluded that there was some undetected variability in the powders.

In general, the results of this investigation indicate that having available a completely reacted, homogeneous LZT powder such as that made by molten salt synthesis is a great help towards obtaining a ceramic with good, reproducible properties; however, empiricism is still required to develop the powder processing and firing conditions necessary to attain that goal.

ACKNOWLEDGMENT

The authors would like to express their appreciation to Dr. G. G. Palmer for graciously making available his long experience in commercial LZT manufacturing, to Dr. S. Bartram for X-ray analysis, to Mr. J. J. Jarek for making electrical measurements, and to Messrs. L. Ezrow and N. Cristello for ceramic fabrication and molten salt synthesis.

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TABLE I

TETRAGONAL LATTICE CONSTANTS

x	a nm	c nm	Other Phases Present
.400	.3977	.4088	
.470	.4030	.4125	
.480	.4031	.4124	
.490	.4040	.4128	
.500	.4048	.4126	
.510	.4051	.4126	
.520	.4055	.4127	
.530	.4054	.4117	Minor Rhombohedral
.540	.4059	.412	"
.550	.4063	.4102	"
.560	.4071	.4101	"
.600	.5746	.7074	Sample Rhombohedral-- Equivalent Hexagonal Parameters Given

X-Ray lattice parameters for LZT Ceramics having the general composition formula

$$Pb_{.94}Sr_{.06}\,(Zr_xTi_{1-x})_{.997}\,Fe_{.003}O_{2.9985}.$$

TABLE II

	LZT	PZT-4
Density - Mg/m^3	7.5	7.5
K_{33}^T (1 KHz)	1200	1300
Tan Δ (1 KHz)	0.002	0.004
k_p	0.52	.58
Mechanical Q	1700	500
d_{33} - 10^{-12} C/N	250	289
% change in K_{33}^T per time decade	-4.0	-5.8
% change in k_p per time decade	-1.6	-2.3
Tan Δ at 0.39 MV/m	0.01	0.04
% change in K_{33}^T at 0.39 MV/m	+4.5	+17

Average values of the properties of an LZT of composition $Pb_{.94}Sr_{.06}(Zr_{.53}Ti_{.47})_{.997}Fe_{.003}O_{2.9985}$ and of PZT-4.

TABLE III

Added Atom	Base Comp.	Density (Mg/m^3)	K^T_{33}	k_p	Tan Δ	$-d_{31}$ $(C/N)x10^{-12}$	Q_M
	A	7.30	1343	.388	.008	84	280
Nb	B	7.35	1788	.468	.009	127	248
	C	7.33	1135	.399	.02	86	142
	A	7.57	1260	.308	.011	61	185
Sb	B	7.55	1807	.385	.014	106	151
	C	7.61	988	.268	.023	51	121
	A	7.55	1160	.287	.006	57	396
Ta	B	7.63	1534	.412	.008	99	275
	C	7.64	962	.498	.011	95	161
La*	B	7.74	1500	.410	.003	88	280

* 1 weight percent added.

One hour post-poling values of properties of several base compositions of LZT with 2.4 atom percent additives. Base compositions:

A, $Pb_{.95}Sr_{.05}(Zr_{.52}Ti_{.48})O_3$; B, $Pb_{.95}Sr_{.05}(Zr_{.54}Ti_{.46})O_3$;

C, $Pb_{.95}Sr_{.05}(Zr_{.56}Ti_{.44})O_3$.

TABLE IV

Powder Batch	Density Mg/m^3	K_o	K^T_{33}	Tan Δ	k_p	d_{31} 10^{-12} C/N
A	7.57	931	1079	.0022	.350	-66
	7.57	939	1084	.0021	.350	-66
	7.57	934	1071	.0018	.334	-62
B	7.62	983	1209	.0022	.498	-102
	7.58	1002	1230	.0022	.502	-104
C	7.59	971	1204	.0023	.483	-99
	7.58	968	1209	.0024	.487	-100
	7.58	971	1200	.0023	.478	-98
	7.59	967	1198	.0026	.483	-99
D	7.59	992	1243	.0024	.514	-109
	7.57	989	1253	.0023	.518	-110
	7.57	1029	1252	.0025	.521	-112
	7.59	1038	1254	.0023	.518	-110
	7.59	1029	1239	.0023	.522	-111
E	7.60	1051	1265	.0024	.521	-111
	7.60	1053	1258	.0024	.518	-110
	7.55	1024	1253	.0024	.521	-111
	7.60	1047	1260	.0026	.522	-111
	7.60	1032	1274	.0025	.529	-114

Values of properties of ceramics made from different powder batches and fired at the same time in a box furnace. Post-poling values measured at one day. Composition of ceramics,

$$Pb_{.94}Sr_{.06}(Zr_{.53}Ti_{.47})_{.997}Fe_{.003}O_{2.9985}.$$

TABLE V

Powder Batch	Density Mg/m^3	K_o	K_{33}^T	Tan Δ	k_p	d_{31} 10^{-12} C/N	d_{33} 10^{-12} C/N
A	7.74	982	1093	.0023	.386	-72	192
	7.74	980	1087	.0024	.386	-72	189
	7.75	980	1076	.0021	.377	-69	181
	7.73	989	1085	.0023	.372	-69	171
B	7.74	1003	1113	.0025	.428	-82	216
	7.76	1003	1131	.0024	.460	-88	234
	7.76	1022	1153	.0024	.472	-92	243
	7.77	1016	1152	.0025	.476	-92	244
	7.76	1021	1135	.0024	.462	-89	235
C*	7.77	1038	1206	.0024	.498	-99	251
	7.74	1034	1208	.0024	.505	-101	258
	7.75	1050	1229	.0023	.515	-104	264
	7.73	1039	1233	.0022	.514	-104	264
	7.73	1041	1214	.0022	.511	-103	264
D	7.75	1030	1143	.0025	.439	-86	220
	7.72	1034	1180	.0025	.483	-96	246
	7.74	1034	1169	.0025	.472	-93	239
	7.71	1030	1168	.0025	.462	-91	227
E	7.78	1059	1229	.0023	.531	-108	270
	7.77	1050	1239	.0021	.524	-107	266
	7.77	1042	1205	.0024	.521	-105	264
	7.77	1058	1243	.0023	.518	-106	265
F	7.70	1057	1062[+]	.0023[+]	.374[+]	-69[+]	185[+]
	7.70	1074	1123	.0024	.436	-84	216
	7.72	1066	1127	.0026	.439	-85	225
G	7.64	984	984	.0022	.303	-55	167
	7.65	981	984	.0024	.324	-59	177
	7.66	995	1008	.0024	.331	-60	173

* Post-poling values measured at 2 days.

[+] Post-poling values measured at 4 days.

Values of properties of ceramics made from different powder batches fired individually in a tube furnace. Post-poling values measured at one day. Composition of ceramics, $Pb_{.94}Sr_{.06}(Zr_{.53}Ti_{.47})_{.997}Fe_{.003}O_{2.9985}$.

TABLE VI

Percent ZrO_2	Density Mg/m^3	K_o	K_{33}^T	Tan Δ	k_p	d_{33} 10^{-12} C/N
1.5	7.59	966	1025	.0024	.338	177
	7.60	972	1041	.0024	.344	178
	7.64	976	1048	.0024	.357	188
	7.60	975	1046	.0025	.353	187
	7.62	975	1053	.0026	.362	195
1	7.74	982	1093	.0023	.386	192
	7.74	980	1087	.0024	.386	189
	7.75	980	1076	.0021	.387	181
	7.73	989	1085	.0023	.372	171
0.5	7.78	1059	1229	.0023	.531	270
	7.77	1050	1239	.0021	.524	266
	7.77	1042	1205	.0024	.521	264
	7.77	1058	1243	.0023	.518	265
0.1*	7.77	1128	1072	.0018	.397	186
	7.80	1119	1111	.0020	.430	213
	7.78	1138	1155	.0020	.469	230

* Powder milled for 1 hour only.

Effect of unreacted ZrO_2 content on the values of properties of ceramics of the composition $Pb_{.94}Sr_{.06}(Zr_{.53}Ti_{.47})_{.997}Fe_{.003}O_{2.9985}$. Post-poling values measured at one day.

TABLE VII

Firing Temp. °C	Density Mg/m^3	K_o	K_{33}^T	Tan Δ	k_p	d_{33} 10^{-12} C/N
1200*	7.37	939	874	.0023	.259	137
	7.37	929	868	.0026	.275	154
	7.34	943	875	.0026	.262	143
1260	7.77	1128	1072	.0018	.397	186
	7.80	1119	1111	.0020	.430	213
	7.78	1138	1155	.0020	.469	230
1305	7.80	1190	1124	.0020	.472	227
	7.82	1140	1173	.0021	.500	251
	7.79	1160	1136	.0020	.468	231

* Post-poling values measured at 4 days.

Effect of firing temperature on the values of the properties of ceramics of the composition $Pb_{.94}Sr_{.06}(Zr_{.53}Ti_{.47})_{.993}Fe_{.003}O_{2.0085}$. Post-poling values measured at one day.

Fig. 1 Agglomerated, molten salt synthesized LZT powder. SEM, 1000X.

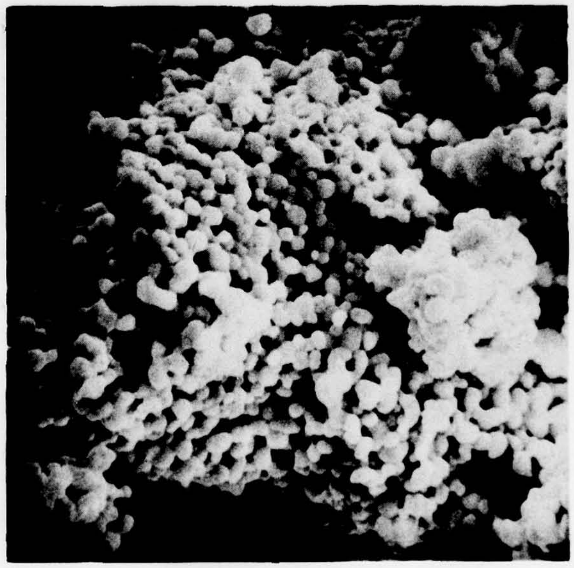


Fig. 2 Detail of LZT powder agglomerate. SEM, 5000X.

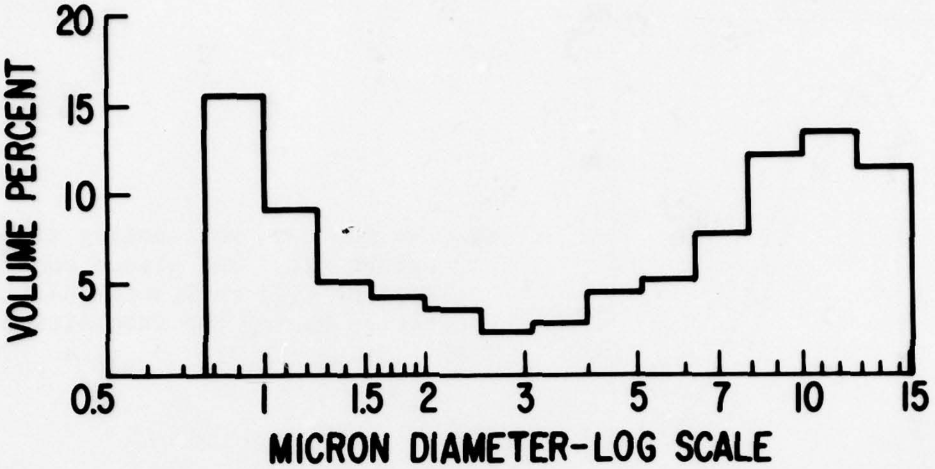


Fig. 3 Particle size distribution typical of those obtained on molten salt synthesized LZT powders using a Coulter Counter.

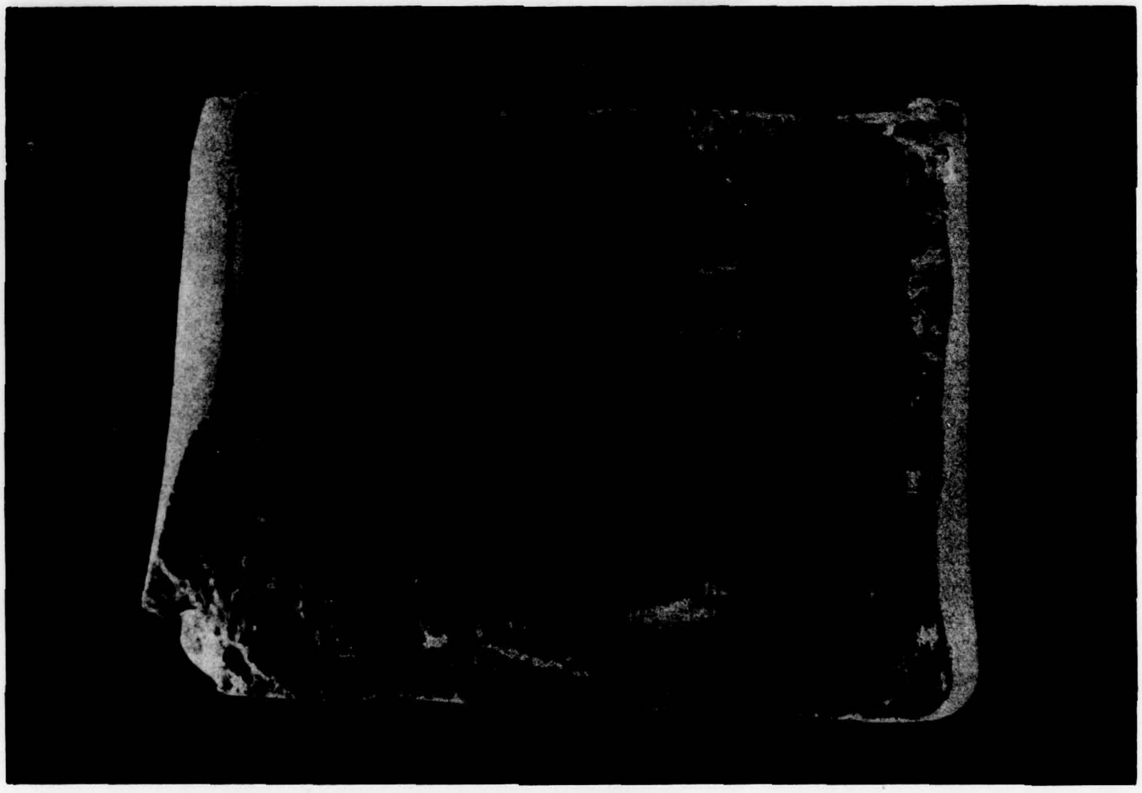


Fig. 4 Sintered sample discs and surrounding, lightly sintered powder as removed from crucible. 3.5X

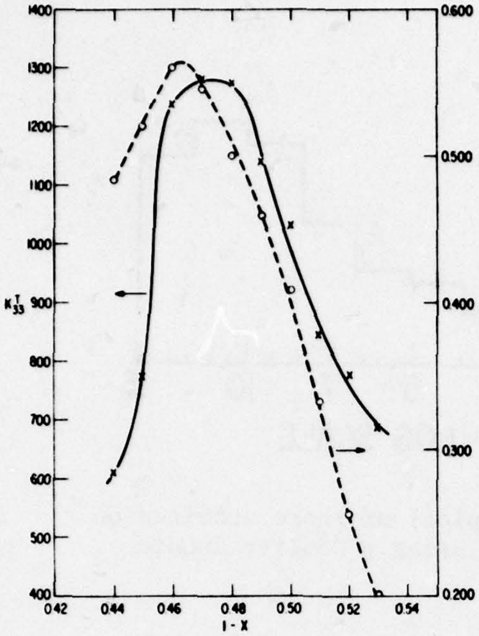


Fig. 5 One hour post-poling dielectric constant (K_{33}^T) and planar coupling coefficient (k_p) versus composition for ceramics having the composition formula $Pb_{.94}Sr_{.06}(Zr_xTi_{1-x})_{.997}Fe_{.003}O_{2.9985}$.

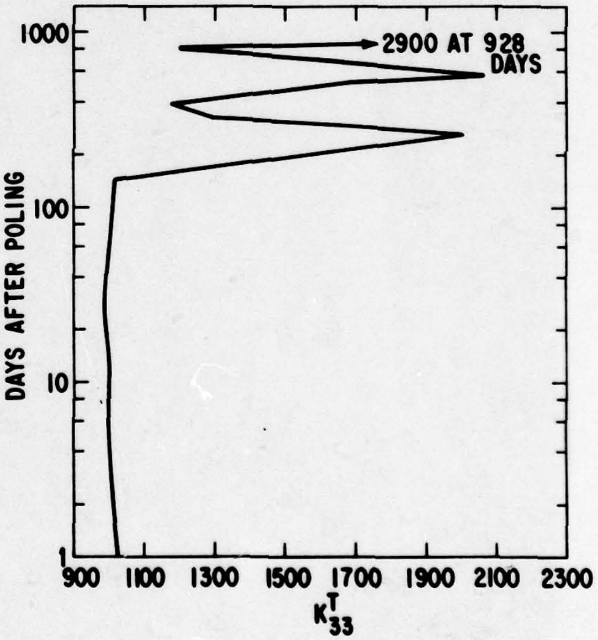


Fig. 6 Aging of the dielectric constant of a specimen of composition $Pb(Zr_{.52}Tr_{.48})_{.97}Fe_{.01}Cr_{.02}O_3$.

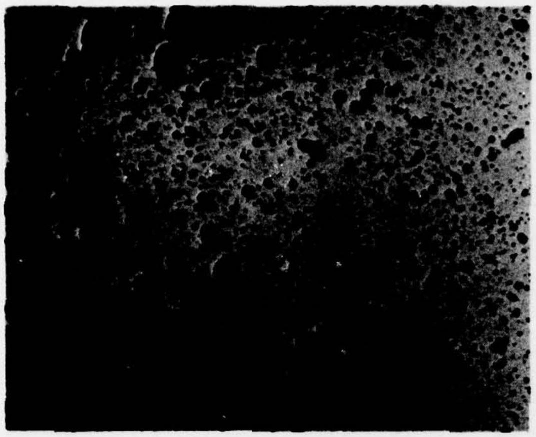


Fig. 7a Polished surface of a ceramic made from Batch C powder fired in the box furnace. 50X.

Fig 7b Same as 7a. 500X.

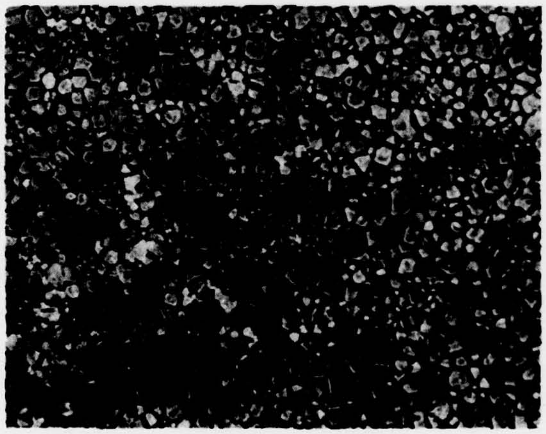


Fig. 7c Same as 7a, etched. 1000X.

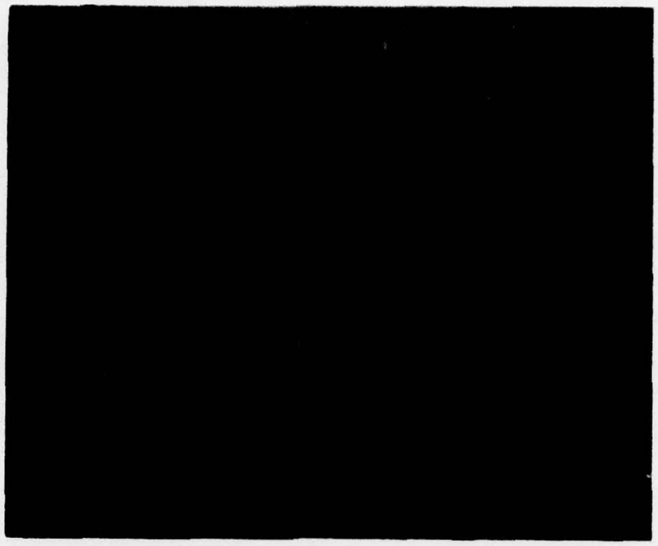


Fig. 8 Polished surface of a ceramic made from Batch A powder fired in box furnace. 500X.

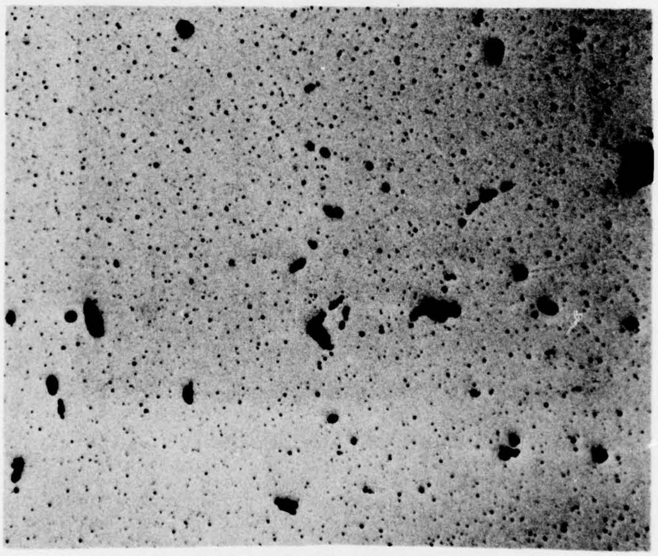


Fig. 9a Polished surface of a ceramic made from Batch C powder fired in the tube furnace. 50X.

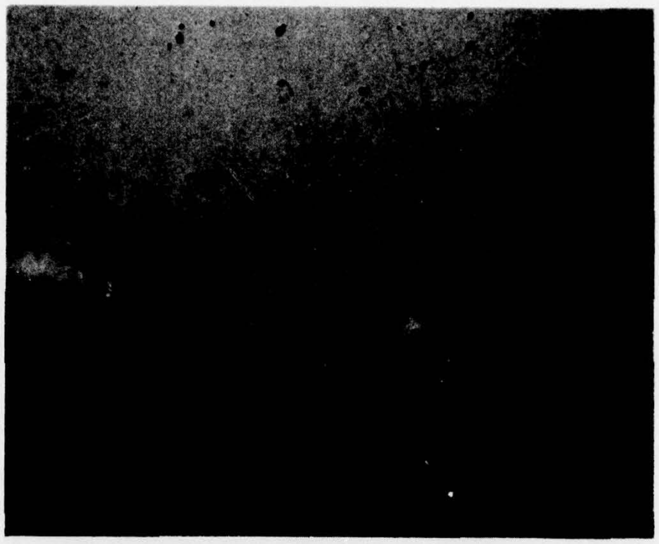


Fig. 9b Same as 9a. 500X.

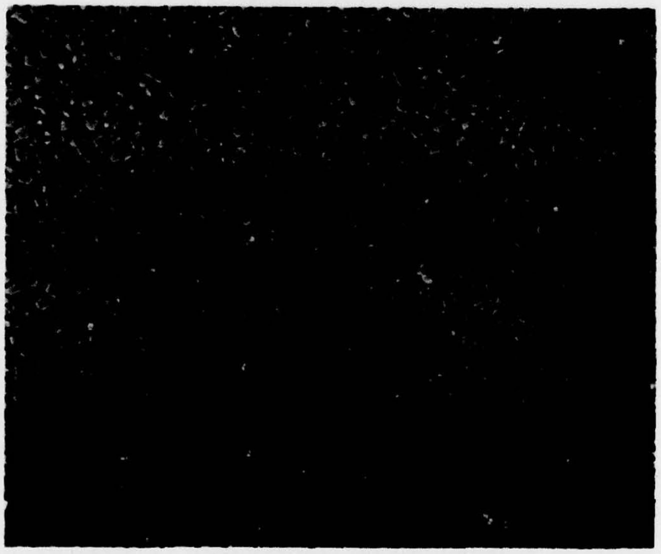


Fig. 9c Same as 9a, etched. 1000X.

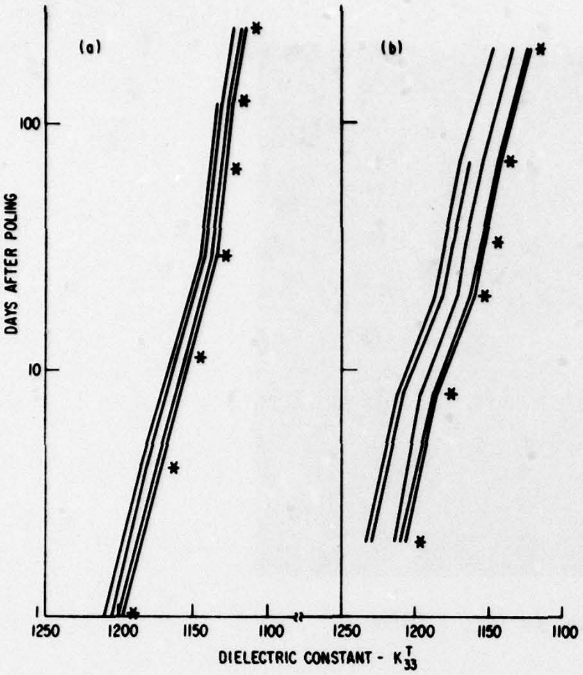
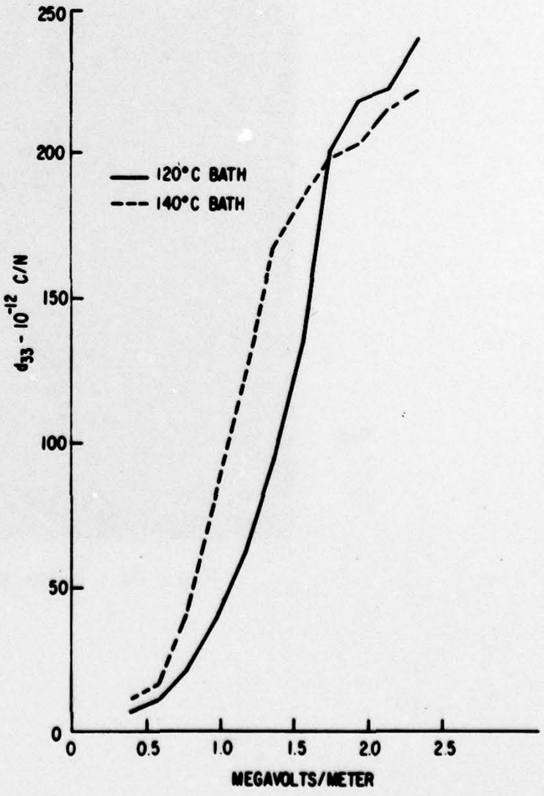


Fig. 10 Aging of the dielectric constant of samples made from Batch C powder and fired in (a) the box furnace, (b) the tube furnace.

Fig. 11 Dependence of the 20 minute post-poling value of the planar coupling coefficient (k_p) on poling field for two poling temperatures. Poling at 120°C with field polarity reversal. Poling at 140°C with constant field polarity.



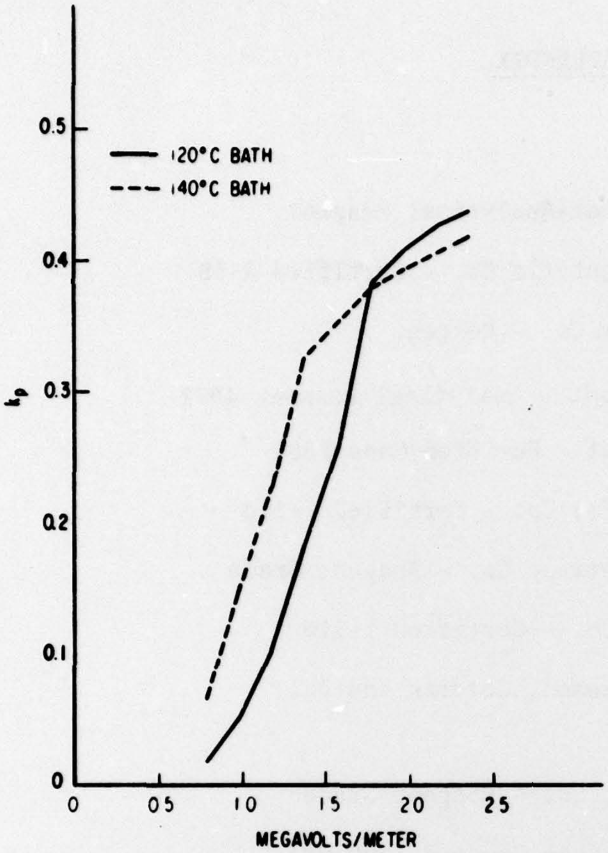


Fig. 12 Dependence of the 20 minute post-poling value of the piezoelectric strain constant (d_{33}) on poling field for two poling temperatures. Poling at 120°C with field polarity reversal. Poling at 140°C with constant field polarity.

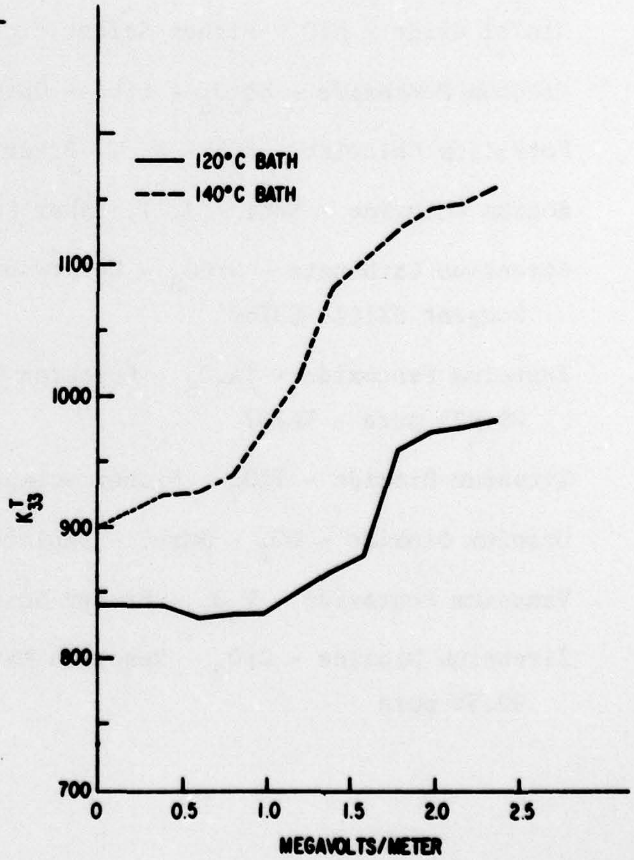


Fig. 13 Dependence of the 20 minute post-poling value of the dielectric constant on poling field for two poling temperatures. Poling at 120°C with field polarity reversal. Poling at 140°C with constant field polarity.

APPENDIX

Reactants Used in LZT Syntheses:

Antimony Trioxide - Sb_2O_3 - Mallinckrodt-Analytical Reagent

Arsenic Trioxide - As_2O_3 - Fisher Scientific Co. - Certified A-59

Bismuth Trioxide - Bi_2O_3 - J. T. Baker Co. - Reagent

Calcium Carbonate - $CaCO_3$ - Mallinckrodt - Analytical Reagent 4072

Chromium Oxide - Cr_2O_3- Allied Chemical - Purified Code 1581

Ferric Oxide - Fe_2O_3 - Fisher Scientific Co. - Certified I-116

Lanthanum Oxide - La_2O_3 - Fisher Scientific Co. - Reagent Grade

Lead Oxide - PbO - Fisher Scientific Co. - Certified I-116

Magnesium Hydroxide - Mg $(OH)_2$ - Mathewson, Coleman and Ball Reagent Powder

Nickel Oxide - NiO - Fisher Scientific Co. - Reagent Grade

Niobium Pentoxide - Nb_2O_5 - Ciba - Optical Grade I (>99.9%)

Potassium Chloride - KCl - J. T. Baker Co. - Reagent

Sodium Chloride - NaCl - J. T. Baker Co. - Reagent

Strontium Carbonate - $SrCO_3$ - Mathewson, Coleman and Ball Reagent SX1010 C3780

Tantalum Pentoxide - Ta_2O_5 - Research Organic/Inorganic Chemical Corp. - 99.99% pure - TA207

Titanium Dioxide - TiO_2 - Fisher Scientific Co. - Certified T315

Uranium Dioxide - UO_2 - Numec - Depleted Ceramic Grade

Vanadium Pentoxide - V_2O_5 - Fisher Scientific Co. - Certified V7

Zirconium Dioxide - ZrO_2 - Reactive Metals Inc. - Reactor Grade 99.5% pure

INDEX OF REPORTS AND PUBLICATIONS

1. "Lead Zirconate Titanate (LZT) Ceramics", Annual Summary Report, J. H. Rosolowski, R. H. Arendt and J. W. Szymaszek, Contract N00014-76-C-0659, June, 1977, Office of Naval Research.
2. "Lead Zirconate Titanate (LZT) Ceramics", Annual Summary Report, J. H. Rosolowski, R. H. Arendt and J. W. Szymaszek, Contract N00014-76-C-0659, June 1978, Office of Naval Research.
3. "Lead Zirconate Titanate Ceramics From Molten Salt Synthesized Powders", R. H. Arendt, J. H. Rosolowski and J. W. Szymaszek, General Electric Co. Report No. 78CRD100, May, 1978.
4. "Lead Zirconate Titanate Ceramics From Molten Salt Solvent Synthesized Powders", Mat. Res. Bull. 14, 703-709(1979).

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