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LEAD ZIRCONIUM TITANATE

Bruce F. Semans

(M. S. Thesis)

March 1968

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CONTENTS

ABSTRACT

I.	INTRODUCTION	1
II.	EXPERIMENTAL PROCEDURE	5
	A. Powder Preparation	5
	B. Sample Preparation	6
	C. Measurement Techniques	8
III.	RESULTS AND DISCUSSION	11
	A. Constant Pressure Runs	11
	B. Pressure Applied at Temperature	12
	1. Density	12
	2. Microprobe Analysis	13
	3. Microscopic Examination	14
	4. X-ray Examination	14
	5. Electrical Measurements	15
IV.	CONCLUSION	16
	ACKNOWLEDGMENTS	17
	REFERENCES	18
	TABLES	20
	FIGURES	25

DENSIFICATION AND ELECTRICAL PROPERTIES OF
LEAD ZIRCONIUM TITANATE

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ABSTRACT

The affect of Al_2O_3 and Bi_2O_3 on the densification and electrical properties of lead zirconium titanate (PZT) solid-solution was studied. Samples were hot pressed at 850°C under 18,000 psi for two hours. Al_2O_3 was shown to form a low melting liquid with PbO that had minimal affect on the densification rate and electrical properties. The $\text{PbO-Al}_2\text{O}_3$ liquid segregated into pockets that did not wet the PZT grain. Bi_2O_3 was shown to lower the temperature at which increased densification occurs as well as lower the coercive field, remnant polarization, and saturation polarization as compared to the undoped material. Although Al_2O_3 was found to segregate, no conclusions on the role of Bi_2O_3 in enhancing the densification process could be made.

I. INTRODUCTION

Lead zirconium titanate solid solutions (PZT) are currently finding varied commercial applications due to their piezoelectric properties. With its relative high Curie temperature and piezoelectric constants, this material is found to be superior to other materials. The applications for piezoelectric materials range from sonar transducers, ultrasonic cleaning devices, strain gages, phonograph pickups, and many other transducer applications.

Intensive research^{1,2,3} has been undertaken to determine physical properties for varying compositions of lead zirconate (PZ)-lead titanate (PT) solid-solutions. The low temperature phases that have been identified are shown in Fig. 1.⁴ Optimal piezoelectric properties have been found near the morphotropic phase boundary between the rhombohedral and tetragonal phases..

Papers^{1,2,5,6} have been published concerning certain additives, in small amounts, that improved sintering characteristics and electrical properties. Usually, however, comparisons between undoped and doped materials are inconclusive, as a second variable (porosity) is present. The percent porosity reported, varies over a wide range. Gerson and Marshall⁷ showed that the measured dielectric strength in porous materials is a function of the porosity, void size, and dimensions of the test sample. They showed a decrease of approximately 40% in the breakdown field with an increase from 10 to 20% porosity. This, at best, makes correlation between measured properties and amounts of doping agents very difficult. At present it appears to be more of an art than a science in selecting suitable doping agents.

There are two possible ways in which impurities can be introduced into a relatively pure raw material. First, they may be added unintentionally during the normal ceramic fabrication processes. Wet or dry milling in conventional containers can lead to the pick up of Al_2O_3 , SiO_2 , or iron oxides, depending on the ball mill composition. Cold pressing operations in iron or steel dies also introduce impurities.

A second method of introducing impurities into ceramic mixes is to purposely add them and determine their affect on measured properties. In order to do this, a standard sample, alike in all respects but for the difference in impurity level, must be obtained. To date such a study has not been made.

Haertling¹ reported properties of the lead zirconate-lead titanate solid solution system containing 2 a/o Bi_2O_3 (7.5 w/o Bi_2O_3) additions. Optimum properties were noted at the morphotropic phase boundary between the rhombohedral and tetragonal ferroelectric phases. Variations of density, remnant polarization, and dielectric constant with mole % PbZrO_3 were given. The effect of temperature, pressure and time on coercive field, remnant polarization, bulk density, and grain size was also investigated. A correlation between the above mentioned electrical properties with average grain size and bulk density was drawn.

Gerson² doped PZT with certain 3-or-5 valence elements (lanthanum, neodymium, tantalum, and niobium). His standard, unmodified ceramic contained 0.5 mole % Sr^{+2} , which he reported as substituting for Pb^{+2} . The modified ceramics were characterized by long periods before relaxation of electrical and mechanical properties took place, a well defined hysteresis loop, and by high electrical and mechanical losses.

Levett³ considered the factors that affected the variations from batch to batch in the manufacture of piezoelectric ceramics. A starting composition of 53 mole % lead zirconate, 47 mole % lead titanate plus an addition of 1.0 w/o of lead niobate was selected. The nominal 53/47 ratio was varied as well as the amount of lead niobate from 0.5 to 1.5 w/o. He concluded that small compositional changes can produce marked changes in both physical and electrical properties of the finished ceramic elements. In all cases, hot pressed bodies exhibited superior mechanical and electrical properties compared to the sintered material.

Seider and Koenig⁸ report calcining and sintering parameters of Nb_2O_5 doped $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ piezoelectrics. Calcining the material twice was found to be beneficial in obtaining a homogeneous starting powder and resulted in a significant increase in density compared to the material calcined only once. Equivalent densities were obtained, with a 95°C reduction in the necessary sintering temperature, when the material calcined twice was used.

Weston⁹ reported an investigation of the preparation and properties of piezoelectric ceramics made from lead zirconate-lead titanate. It was found that the compositional reproducibility achieved was poor and the properties of the ceramics suffered from the presence of substantial amounts of impurities introduced during ball milling of the constituents. Pneumatic milling was successful in promoting good sintering properties without excessive impurity pick-up. Reproducibility was not increased, however, over traditional methods of milling.

Jaffe⁴ reported the ferroelectric and piezoelectric properties of polycrystalline doped solid solutions of lead titanate and lead zirconate.

Major variations in dielectric and electromechanical properties obtained were shown. He also presented a theory explaining these variations on the basis of a lattice vacancy-hole equilibria.

Kulcsar⁵ reported the properties of lead zirconium titanate with small amounts of lanthana, neodymia, niobia, or tantalum added. The modified ceramics showed piezoelectric planar coupling coefficients of about 0.50 as compared to 0.35 for BaTiO_3 and substantially increased dielectric constants up to a value of 1545. The pure standard used during the experiments was $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$.

Tien and Carlson⁶ investigated the effect of additives on the properties of lead titanate. It was found that all additives, Li_2O , Na_2O , K_2O , Ag_2O , ZnO , CdO , Y_2O_3 , Al_2O_3 , Ga_2O_3 , Sc_2O_3 , KF , CaF_2 , MgF_2 , MgCl , LiF , and LiCl , produced samples that were dense and mechanically strong. This is in contrast to the very porous and fragile specimens previously reported for pure PbTiO_3 . However, due to the minute additive concentrations employed, no attempt was made to ascertain the role of the additive in regard to sintering behavior.

The purpose of this study was to investigate the effect of (1) 0.5 w/o Al_2O_3 to simulate indirect doping, and (2) 0.5 w/o Bi_2O_3 to simulate direct doping additions, on densification rate during hot pressing, microstructure, and electrical properties of $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$.

II. EXPERIMENTAL PROCEDURE

A. Powder Preparation

Reagent grade lead oxide,^{*} reagent grade titanium dioxide,^{**} and reactor grade zirconium dioxide^{***} were used in preparing the composition $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$. A 400 gram batch was weighed on an analytical balance and put in a glass quart jar. To this, 500 cc isopropyl alcohol was added. Mixing was done on a rotary mixer using hard rubber cylinders approximately 3/8" diameter by 1/2" long to insure complete mixing.

To insure that settling of the components did not occur during drying, the alcohol mixture was boiled in a water bath while being stirred by a glass rod. No visual evidence of segregation was evident after all the alcohol had been evaporated.

The dried powder was then cold pressed, under 6000 psi, into 25-30 gram 3/4" diameter slugs. The PZT pellets were put into a platinum crucible that was covered and heated in air to 800°C for 100 hours. The calcined pellets were then crushed in a Lucite mortar and pestle to minimize contamination. The powder was screened to -270 to 325 mesh particles to insure uniform starting particle size. This does not necessarily classify the starting grain size, as agglomeration probably took place. The powder was X-rayed in order to determine the presence of any unreacted constituents. No detection of PbO , ZrO_2 , or TiO_2 was detected which indicated a homogeneous starting powder.

* Hammond Lead Products

** Fisher Scientific Company

*** Wah Chang Corporation

Laboratory experience had shown a small amount of plastic could be picked up during the particle size reduction. Therefore, the calcined powder was heated to 350°C to remove the slightest trace of this impurity. No residue was evident and it is assumed all plastic was removed by oxidation.

The batch was then divided into four equal amounts; to the first 0.5 w/o Bi_2O_3^* was added; to the second 0.5 w/o $\text{Al}_2\text{O}_3^{**}$ was added; to the third 0.5 w/o the eutectic composition of Bi_2O_3 - Al_2O_3 (approx. 4 mole/o Al_2O_3) was added; the fourth was used as the standard. Each of the four batches was mixed in isopropyl alcohol contained in a glass jar with hard rubber tumblers. This mixture was dried as before.

Semi-quantitative spectrographic analyses were run on each of the four batches of powder (Table I).

B. Sample Preparation

The hot pressing assembly is shown in Fig. 2. The sample was heated by a Kanthal wound, resistance heating coil. All runs were made in pure oxygen at one atmosphere pressure. The temperatures were measured by Pt-Pt 10% Rh thermocouples and monitored on a multipoint recorder. A control run was made monitoring the temperature of the sample, support column and heating coil. The sample temperature was measured by placing a thermocouple inside the specimen. It was assumed that a constant temperature difference would be maintained between the sample and the

* General Chemical Division of Allied Chemical Company

** Linde A, Linde Company, a Division of Union Carbide Corporation

support column during all subsequent runs that followed the same procedure. The temperature was controlled by an automatic temperature controller driving a saturable core reactor which in turn varied the power to the Kanthal coil.

Each sample to be hot pressed weighed approximately 10.5 grams and was cold pressed in a 3/4" diameter die at 6000 psi prior to hot pressing. A 5 mil platinum foil ring, spot welded, was then made to fit the exact dimensions of the cold pressed sample. Five mil platinum foil was then placed above and below the sample which insured a good seal against the loss of PbO during heating. Nickel foil, 5 mils thick, was placed above and below the platinum in order to eliminate any sticking between the platinum foil and Al_2O_3 support column. The assembly was placed between two 99.5% Al_2O_3 plugs 2" in diameter by 2" long. During hot pressing, the entire column expansion or contraction was monitored by a linear variable differential transformer and recorded on a singlepoint recorder as a function of time.

Two series of hot pressing runs were made. In the first, a pressure of 1000 psi or 3000 psi was applied at room temperature. The sample was heated manually to approximately 200°C then held constant while the sample and the supporting column came to thermal equilibrium. The temperature was then increased at a constant rate of 10°C/min. The expansion of the column was recorded continuously during this process. A reproducible linear expansion was obtained from the 200°C equilibrium position, until a rapid increase in the rate of densification of the sample occurred. The temperature at which the compaction of the sample exceeded the expansion of the column was noted for each of the four batches. This temperature

shall be referred to as T_{INC} throughout the rest of this paper. After the increased rate of densification for each sample was reached, the pressure was released to a holding pressure of 100 psi while the sample cooled to room temperature.

In the second series, a holding pressure of 100 psi was applied at room temperature to insure column alignment. The pressure was maintained constant while the temperature was increased manually to 200°C. After thermal equilibrium was reached by the support column, the temperature was increased at the rate of 10°C/min. After a short period of thermal stabilization at a temperature just in excess of T_{INC} for each sample, a pressure of 18,000 psi was applied and held constant for two hours. During the two hours at pressure, the sample compaction was recorded. For all runs the compaction rate slowed to 10^{-4} in/min after two hours pressure. All hot pressing showed good reproducibility.

C. Measurement Techniques

Density measurements were made by the displacement method using mercury or ethyl alcohol as the liquid medium. Samples weighing from 3 to 6 grams were used. Specimen grain size was obtained by mounting a section of each sample in clear casting resin. The sections were ground on 2/0, 3/0, 4/0 emery polishing paper followed by lapping on a 6 micron diamond impregnated wheel and a finishing polish with a water slurry of either Linde A alumina or cerium oxide. Etching was done at 0°C in 35% HCL solution with 3 drops concentrated HF added per 100 ml of solution.

Microprobe data was obtained from a carbon coated polished section of each sample. Aluminum K_{α} and bismuth M_{β} were the characteristic

lines used in the analysis. Intensities were compared to standards, while background was obtained from the undoped material. Difficulties were realized in locating concentrations of Bi^{+3} in the as produced samples. This can be appreciated by the fact that the beam of a microprobe is approximately $1\text{-}2\mu$ in diameter. Since the sample contained grains of approximately this size, the analysis could not distinguish between grains and grain boundaries. Specimens of the as pressed standard PZT and of the bismuth doped material were therefore heat treated in order to grow larger grains that could be quantitatively analyzed for bismuth. The standard sample was wrapped in platinum foil and heated in air to 1200°C for one hour. A grain size of $10\text{-}20\mu$ was realized after this treatment. After a similar treatment the bismuth doped sample showed a minimal amount of grain growth. The bismuth doped sample was heated a second time to 950°C for 10 hours followed by a one-hour period at 1150°C . An average grain size of 10μ was obtained after this operation. This piece was then examined under the microprobe.

Ferroelectric loop data (remnant polarization, saturation polarization, and coercive field) were obtained on a D-C Looper as depicted in Fig. 3. The electrodes applied were silver conductive paint,* that had been baked under infrared heat. During application of the voltage, the sample was immersed in silicon oil to reduce surface conduction. All compositions showed a tendency to be electrically "leaky" samples, therefore not exhibiting a square hysteresis loop. Goodman¹⁰ showed there was

* Du Pont No. 4817

not a linear relationship between current and voltage in samarium doped BaTiO_3 . It is felt that a decrease in resistance as high voltages are applied produces a "leaky" sample and the destruction of square hysteresis loops. In order to obtain measurements of electrical properties of the samples produced, a slow $1/4$ cpm was used in applying the voltage causing polarization to occur in the sample.

III. RESULTS AND DISCUSSION

A. Constant Pressure Runs

Figures 4 and 5 show the change of T_{INC} in Bi_2O_3 doped samples as compared to the standard PZT. Table II indicates the temperature at which increased densification occurred for all materials tested. As is evident, the effect of Al_2O_3 is negligible at these temperatures and pressures. Bismuth oxide, on the other hand, shows a marked lowering of the temperature at which increased densification occurs. A decrease of $70^\circ C$ is apparent between the standard or the Al_2O_3 doped samples and the Bi_2O_3 doped samples.

Kingery¹¹ describes the mechanisms of densification that occurs during the firing of ceramics. These pertain to changes in grain size and shape, changes in pore size, and changes in pore shape. The mechanisms that are operative during hot pressing may be grouped under solid-state reactions and reactive liquid densification. In the PZT system of interest, the possibility of either of the above seems evident from the data collected and the available references.

The partial phase diagram¹² for the system $PbO-Bi_2O_3$ indicates the existence of a low melting liquid phase at approximately $730^\circ C$. It is known, that during the hot pressing of PZT, PbO can be lost to the atmosphere due to its high vapor pressure. It is reasonable to assume that in a porous compact, as all ceramics initially are, that PbO vapor would initially be expelled at the surface of each grain. This is proposed by Gerson and Jaffe¹³ to produce a defect structure causing p-type semiconduction. The formation of a low melting liquid, between the PbO vapor

vapor and the Bi_2O_3 impurity, would explain the decrease of temperature where increased densification occurs. Such a liquid would wet the PZT grains and form a thin film at the grain boundaries. The presence of such a second phase would allow the solution and reprecipitation of solids thus aiding material transport.

The second mechanism that could be operative is the enhancement of diffusion in the individual grains due to the substitution of Bi^{+3} for Pb^{+2} , Zr^{+4} , or Ti^{+4} . References 14 and 15 show that BiO is thermodynamically less stable than Bi_2O_3 at these temperatures. For the reaction: $\text{Bi}_2\text{O}_3 \rightarrow 2\text{BiO} + 1/2 \text{O}_2$, the heats of reaction are +27,000 at 500°K, +21,850 at 850°K, and +16,000 at 1100°K. It is shown that Bi_2O_5 decomposes by the loss of an oxygen at 150°C. Therefore, it is felt that the presence of Bi^{+3} is most likely. Haertling¹ states that bismuth substitutes for Zr^{+4} or Ti^{+4} . The radius of the available hole for the tetravalent ion is 0.71Å. Taking into consideration ionic radii, Table III, it is found that the difference between the radius of Bi^{+3} and the radius of the available hole is greater than the 15-20% margin that is usually assumed in substitutional solid solution. Therefore, it is felt the substitution of two Bi^{+3} for three Pb^{+2} with the creation of a cation vacancy is most likely. During the hot pressing operation, the increase in number of cation vacancies could enhance densification and explain the behavior observed in Bi_2O_3 doped PZT.

B. Pressure Applied at Temperature

1. Density

Samples produced by application of pressure at temperature were

found to be translucent. During the pressing of the sample the thin platinum foil ring was not broken, showing that with a low height to diameter ratio material constraint is more important than external radial constraint. The sample densities are given in Table IV. A comparison of the measured density to the theoretical density was not made since the presence of a second phase was shown in all samples. It is evident that the effect of the additives on final density is minimal with this type of forming process.

2. Microprobe Analysis

Microprobe data showed the presence of aluminum in pockets, high in lead concentrations, throughout all samples. As is evident from the spectrographic analysis there are trace amounts of Al_2O_3 in all samples in addition to that intentionally added. The phase diagram¹¹ for $\text{PbO}-\text{Al}_2\text{O}_3$ shows a eutectic temperature of 865°C . During the heating operation PbO vapor combines with Al_2O_3 and forms a second phase. This liquid does not wet the PZT grains resulting in its transport and accumulation into segregated pockets thus showing no significant effect on densification (Figs. 6-9).

Initial microprobe data indicated an evenly distributed concentration of bismuth throughout the bismuth doped sample. The measurement, however, on $1-3\mu$ grain material with a $1-2\mu$ beam could not give conclusive data. The heat treated samples, with larger grain size (Figs. 10,11) were then examined with the result being that a uniform Bi^{+3} concentration was found. No grain boundary segregation was found, therefore bismuth must have diffused into the PZT lattice. These data obtained after an 1150°C heat

treatment unfortunately does not positively conclude that the mechanism of diffusion is occurring at the low hot pressing temperature of formation and therefore the possibility of a liquid phase must still be considered.

3. Microscopic Examination

The polished section, before etching, showed an even distribution of closed porosity with individual pores less than one micron in diameter. It was also possible to identify easily the second phase of $\text{PbO-Al}_2\text{O}_3$. After etching, it was found that the sample was heterogeneous. The specimen was attached preferential giving a spotty effect to the microstructure. The areas that were slowly etched gave a traditional grain surface with grain sizes ranging from 1-3 microns (see Figs 12-15). By lowering the temperature of the etchant and decreasing the amount of HF, it was possible to ascertain that the areas that were more rapidly attached were areas of very fine grained material. Therefore, due to the presence of an increased number of grain boundaries, the material was preferentially etched.

4. X-ray Examination

X-ray examination of the calcined powder before hot pressing, of the produced sample after pressing, and of powder obtained from the high density sample indicated: (1) no change in composition occurred during hot pressing; (2) there was a slight degree of preferred orientation. The (001) plane was aligned perpendicular to the pressing direction. This indicates that as the sample is cooled through its Curie temperature, there is a tendency for the polarized direction to be in the unconstrained direction as opposed to the radial direction.

5. Electrical Measurements

Values for coercive field, remnant polarization, and saturation polarization are given in Table V. As is evident, the Bi_2O_3 additive has a marked affect on all the measured values. The values given for bismuth additive samples are in good agreement with the published data of Haertling.²

IV. CONCLUSION

High density, optically translucent lead zirconium titanate can be produced by hot pressing techniques. Additions of Al_2O_3 form a low melting lead aluminate liquid that has a minimal effect on densification rate and electrical properties at the temperatures and pressures used. The presence of this second phase was evident in microscopic and microprobe examination. Additions of Bi_2O_3 show a marked lowering of the temperature at which an increased rate of densification occurs. This can be explained by either the formation of a low melting $\text{PbO-Bi}_2\text{O}_3$ liquid or by the increase in cation vacancies that would enhance the densification rate. Coercive field, remnant polarization, and saturation polarization are lowered with Bi_2O_3 additives as compared to the undoped and Al_2O_3 doped material. After heat treating the sample to 1150°C a uniform distribution of bismuth occurred throughout the sample indicating a solid solution of bismuth in the perovskite grains.

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Table I. Spectrographic Analysis of
Calcined Powders

	Standard	Bi ₂ O ₃ Doped	Al ₂ O ₃ Doped	Bi ₂ O ₃ & Al ₂ O ₃ Doped
Al	0.03%	0.02%	0.45%	0.1%
Si	.07	.05	.05	.04
Ba	.07	.07	.06	.07
Bi	.01	.5	.01	.4
Fe	.01	< .01	.01	.01
Mg	.002	.003	.002	.002
Cu	< .002	< .002	< .002	< .002

Table II. Temperature Variation Where Increased Densification
Occurred for Differently Doped PZT

Sample	Constant pressure applied (lbs/in ²)	T _{INC} (°C)
Standard	1000	810
Bi ₂ O ₃ doped	1000	725
Al ₂ O ₃ doped	1000	810
Bi ₂ O ₃ & Al ₂ O ₃ doped	1000	755
Standard	3000	775
Bi ₂ O ₃ doped	3000	710
Al ₂ O ₃ doped	3000	760
Bi ₂ O ₃ & Al ₂ O ₃ doped	3000	730

Table III. Ionic Radii and Coordination Number
for Various Ions

Ion	Coordination number	Ionic radii (Å) ^o
Pb ⁺²	12	1.30
Bi ⁺³	12	1.01
Bi ⁺³	8	.96
Zr ⁺⁴	8	.82
Ti ⁺⁴	8	.71

Table IV. Variation in Density as a
Function of Additive Used

Sample	Measuring Medium	
	Alcohol	Mercury
Standard	7.94 g/cc	7.67 g/cc
Bi ₂ O ₃ Doped	7.95	7.83
Al ₂ O ₃ Doped	7.91	7.70
Bi ₂ O ₃ & Al ₂ O ₃ Doped	7.95	7.63

Table V. Variation of Electrical Properties, (Coercive Field, Remnant Polarization, Saturation Polarization), Function of Additive

Sample	E_c , volts/mil	P_r , $\mu\text{coul}/\text{cm}^2$	P_s $\mu\text{coul}/\text{cm}^2$
Standard	63.4	28.6	35.4
Bi_2O_3 doped	37.4	10.9	14.3
Al_2O_3 doped	55.0	16.6	19.2
Bi_2O_3 and Al_2O_3 doped	34.5	10.0	13.7

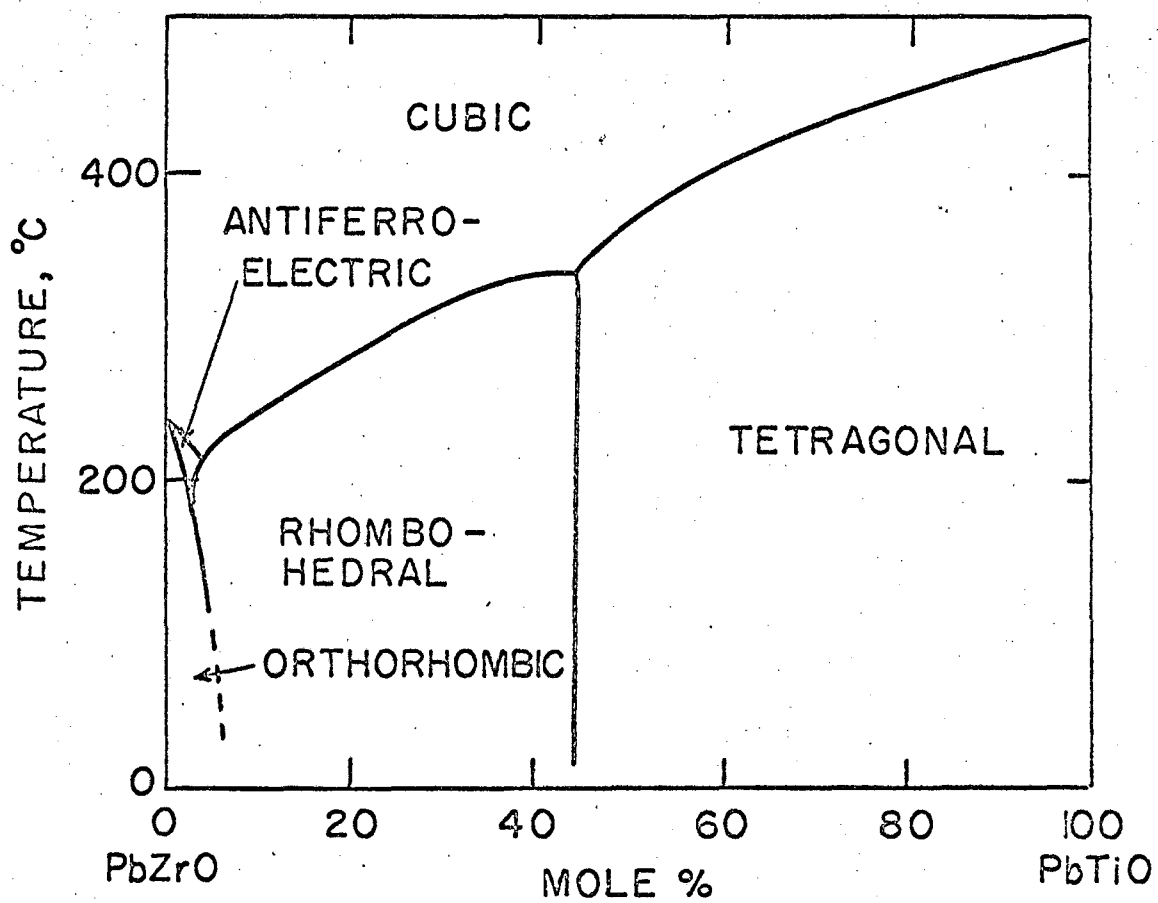


Fig. 1. Low temperature phase system of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ⁷

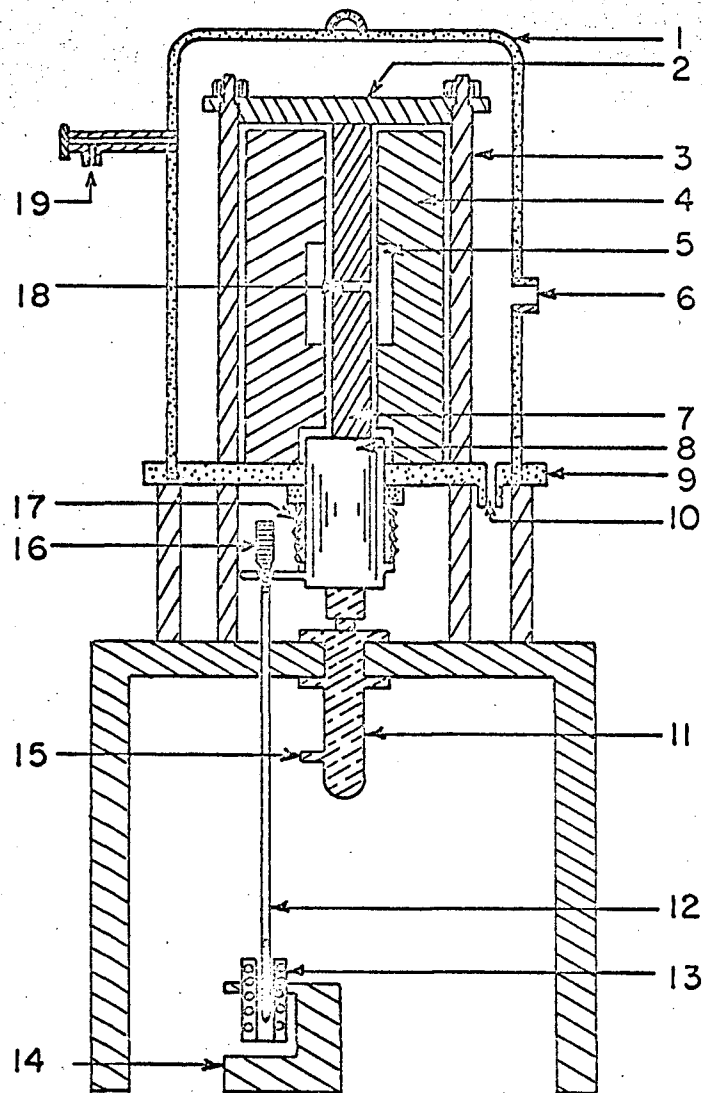


Fig. 2. Atmosphere hot pressing assembly

- | | |
|---------------------------|---|
| 1. Vacuum cover | 10. Vacuum port |
| 2. Top yoke | 11. Hydraulic ram |
| 3. Load bearing column | 12. Metal rod |
| 4. Refractory brick | 13. Linear variable
differential transformer |
| 5. Heating coil | 14. Support block |
| 6. Sight window | 15. Pressure inlet |
| 7. Alumina support column | 16. Micrometer |
| 8. Copper plunger | 17. Bellows |
| 9. Bottom support plate | 18. Specimen |
| | 19. Air inlet |

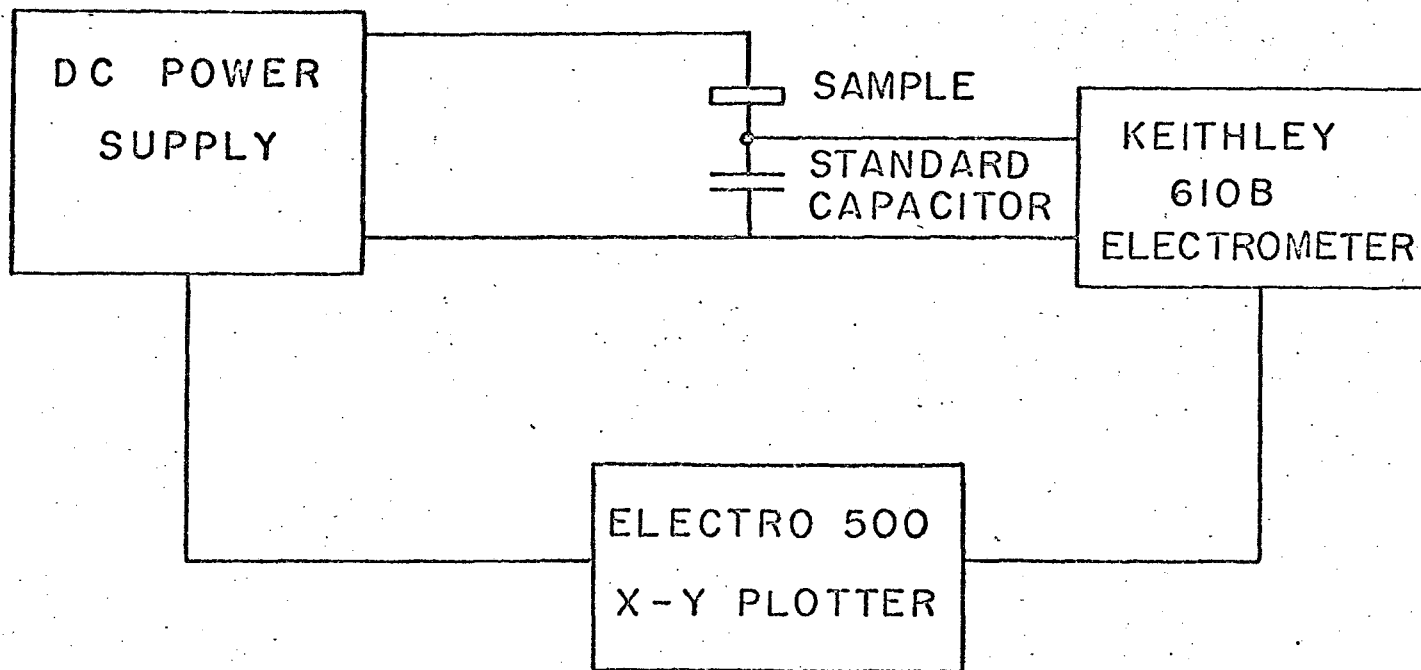


Fig. 3. DC Looper

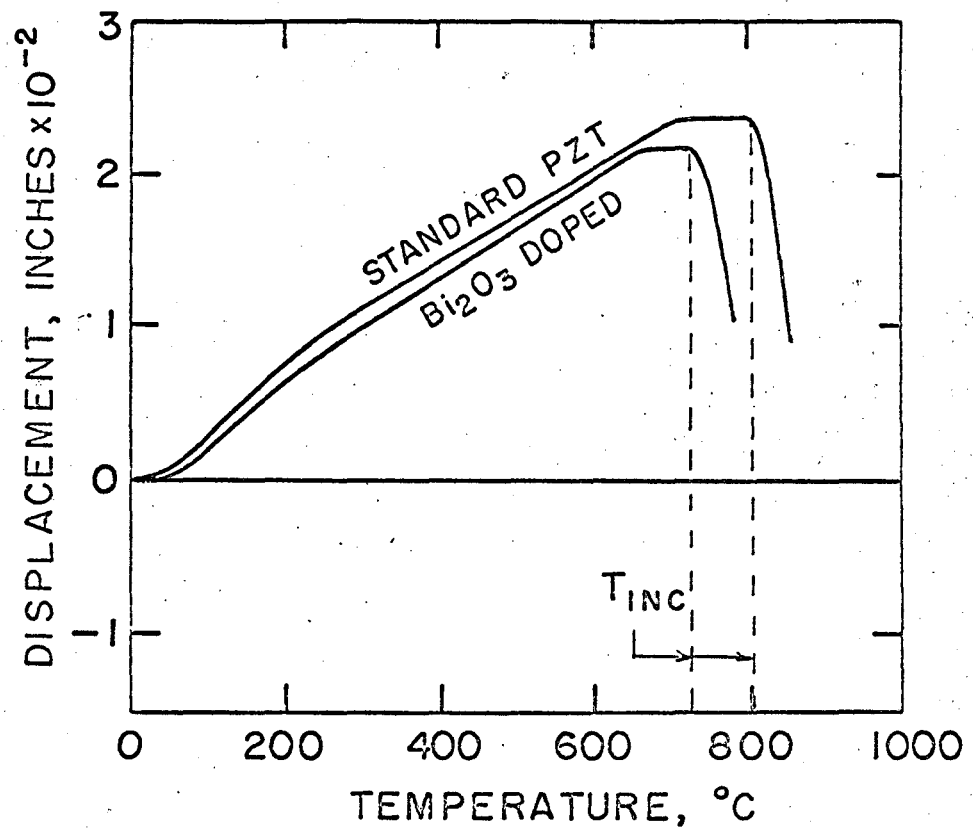


Fig. 4. Displacement temperature for standard and Bi_2O_3 doped PZT under constant pressure of 1000 psi.

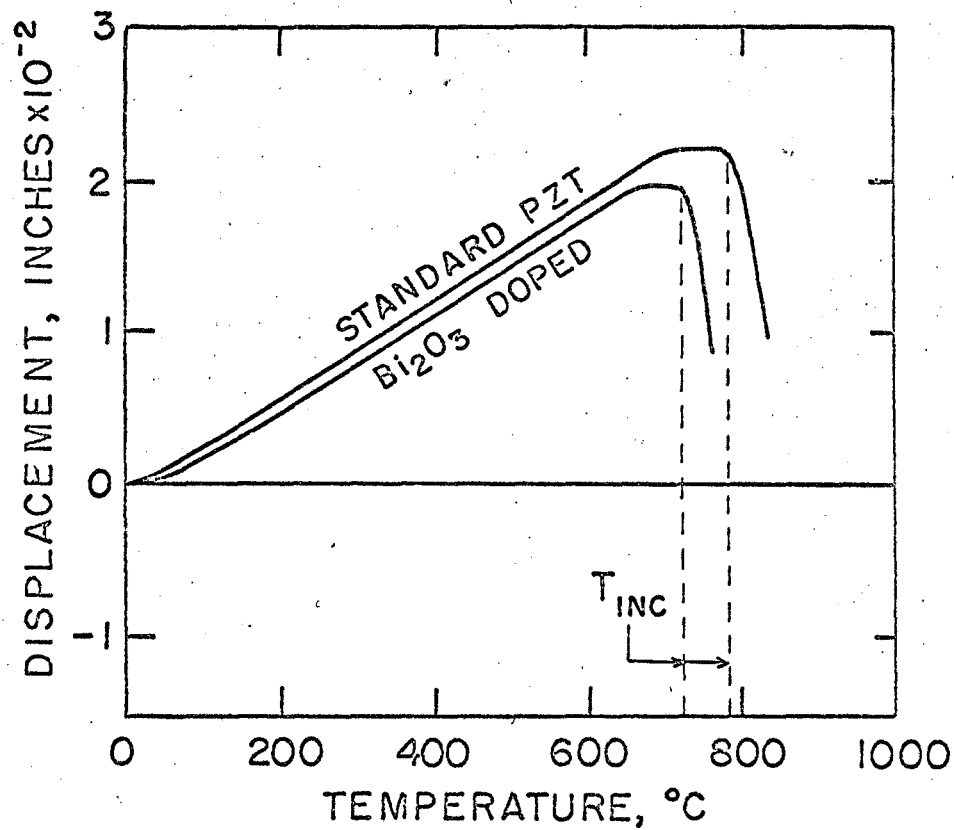
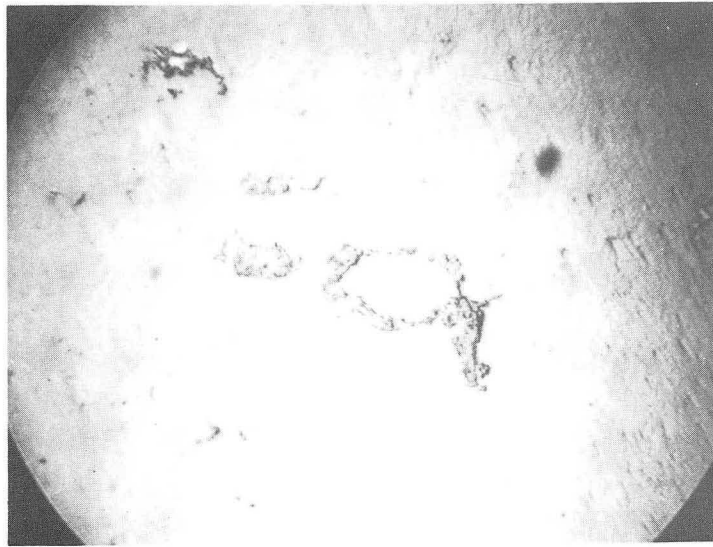


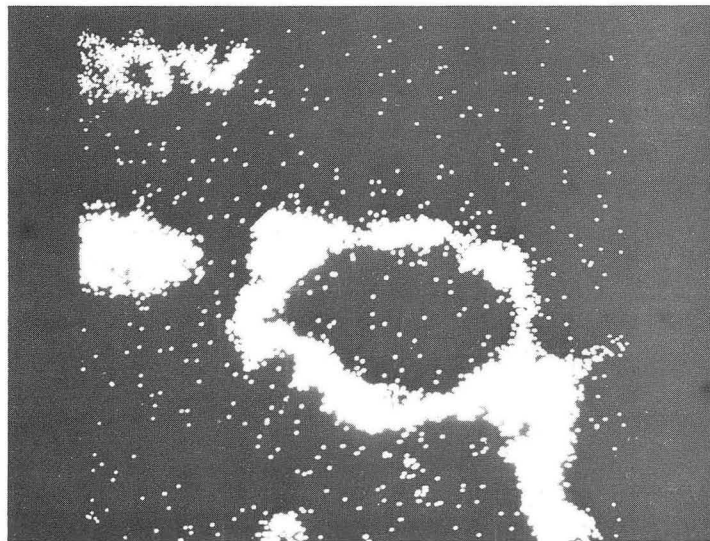
Fig. 5. Displacement temperature for standard and Bi_2O_3 doped PZT under constant pressure of 3000 psi.



50μ

XBB 683-1201

Fig. 6 Photomicrograph showing Al_2O_3 pockets in Al_2O_3 doped materials.



20μ

XBB 683-1200

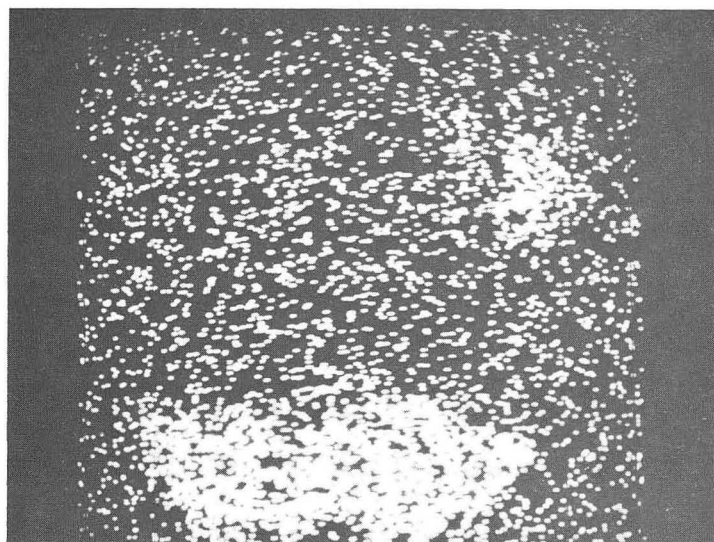
Fig. 7 Aluminum concentration in the specimen shown in Fig. 6.
Microprobe scan of aluminum K_{α} .



50 μ

XBB 683-1202

Fig. 8 Photomicrograph showing Al₂O₃ pockets in undoped material.

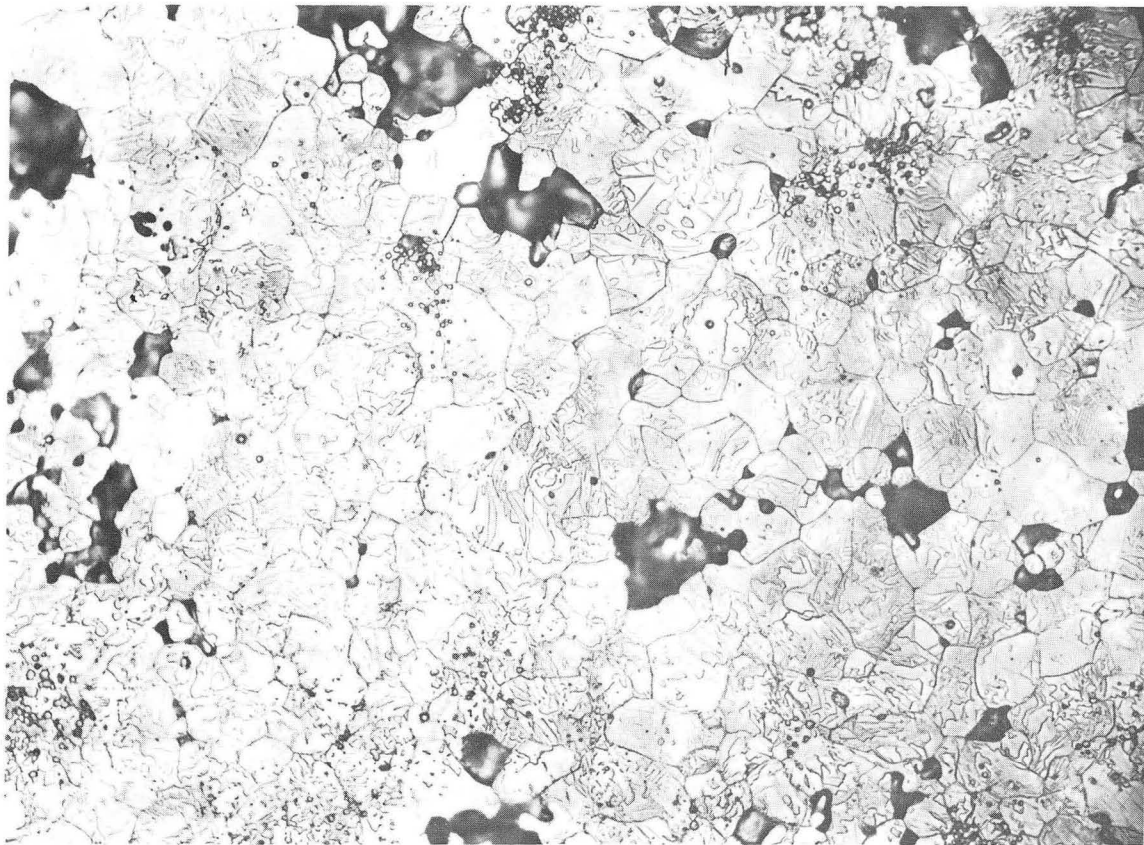


20 μ

XBB 683-1203

Fig. 9 Aluminum concentrations in the specimen shown in Fig. 8. Microprobe scan of aluminum K_α*.

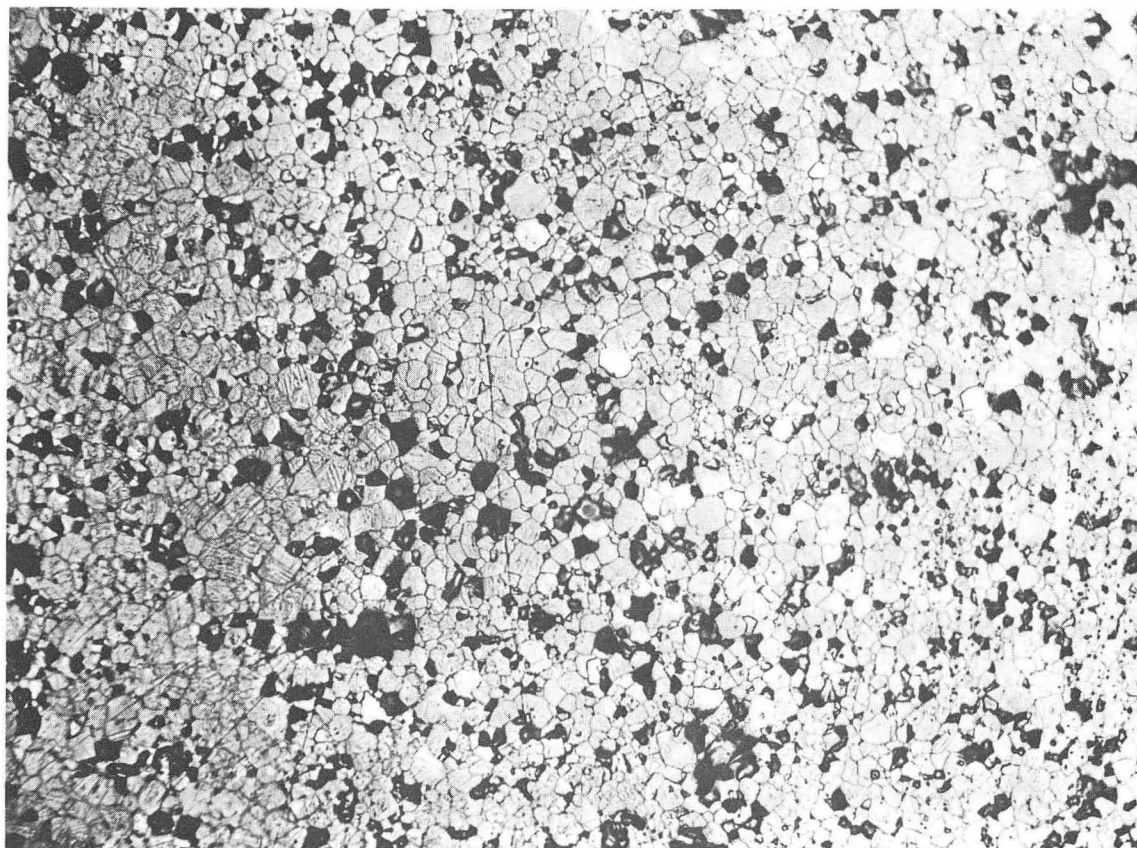
* Increased background due to increased number of scans used.



20μ

XBB 683-1195

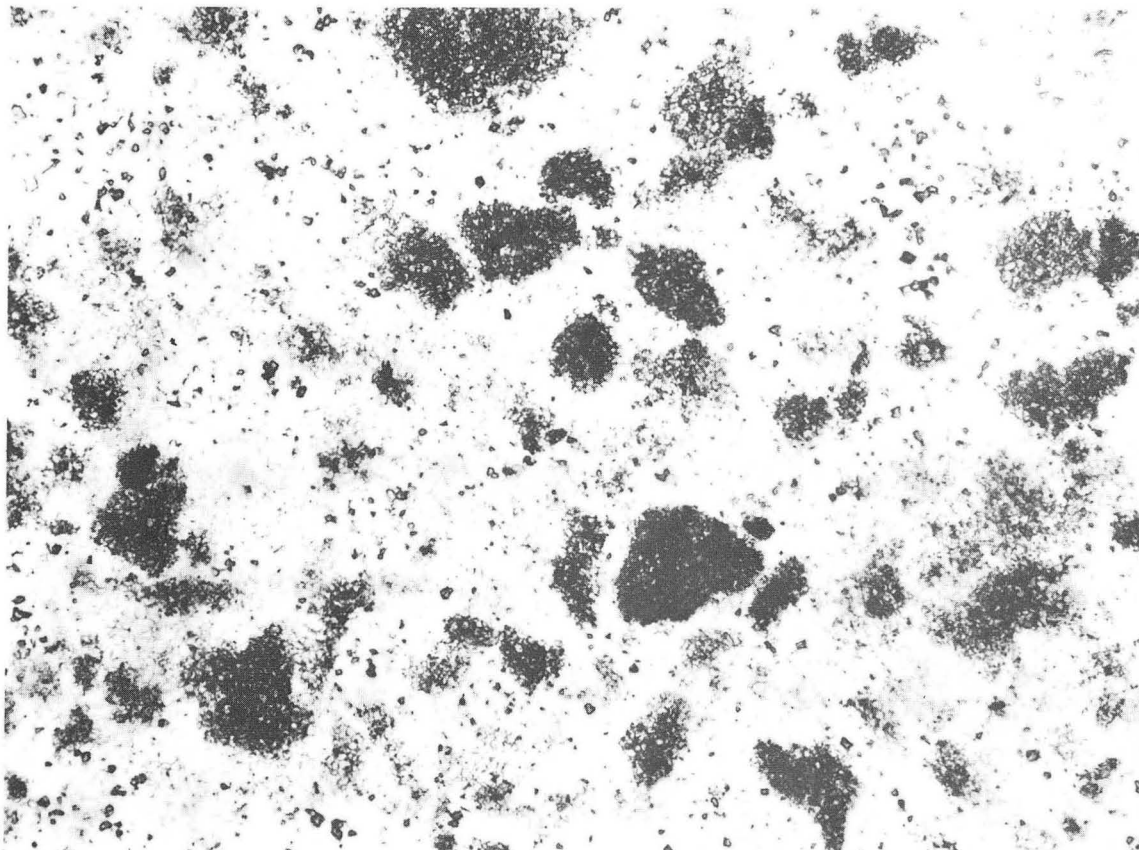
Fig. 10 Photomicrograph of heat treated
standard PZT (etched).



20μ

XBB 683-1194

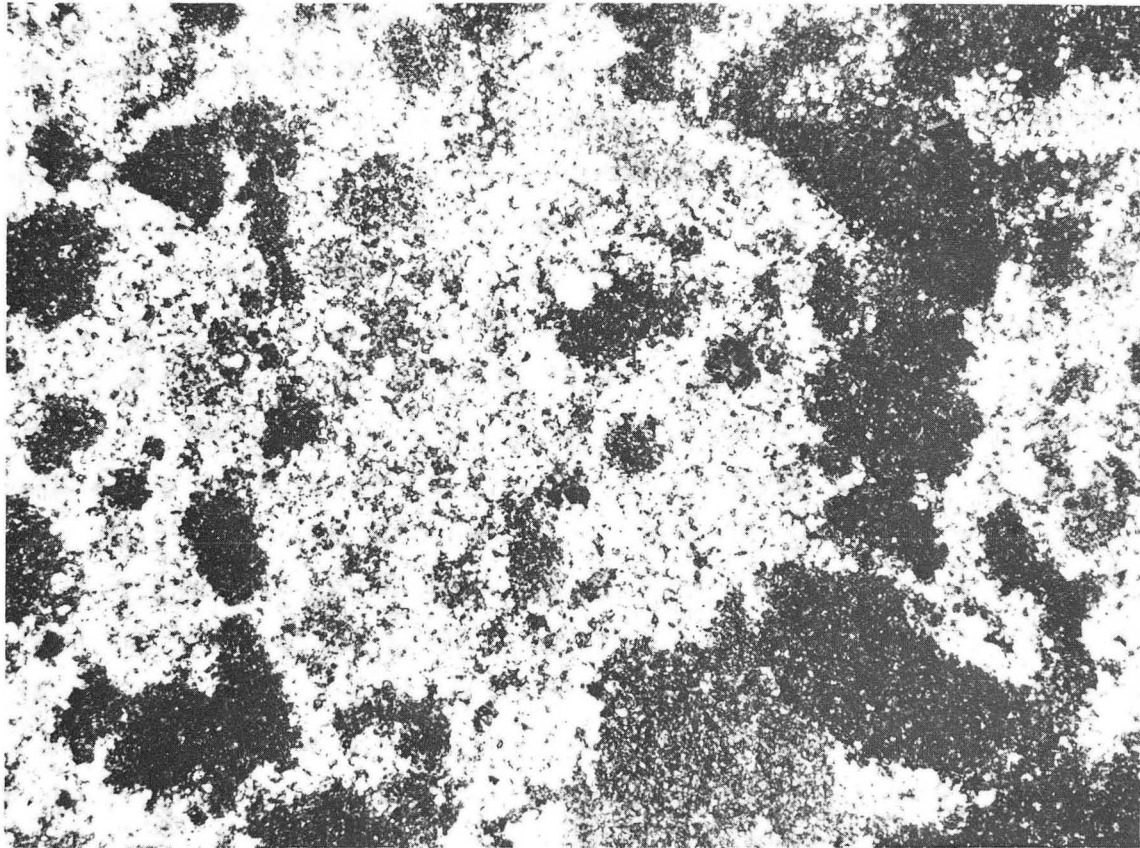
Fig. 11 Photomicrograph of heat treated
 Bi_2O_3 doped PZT. (etched).



20 μ

XBB 683-1197

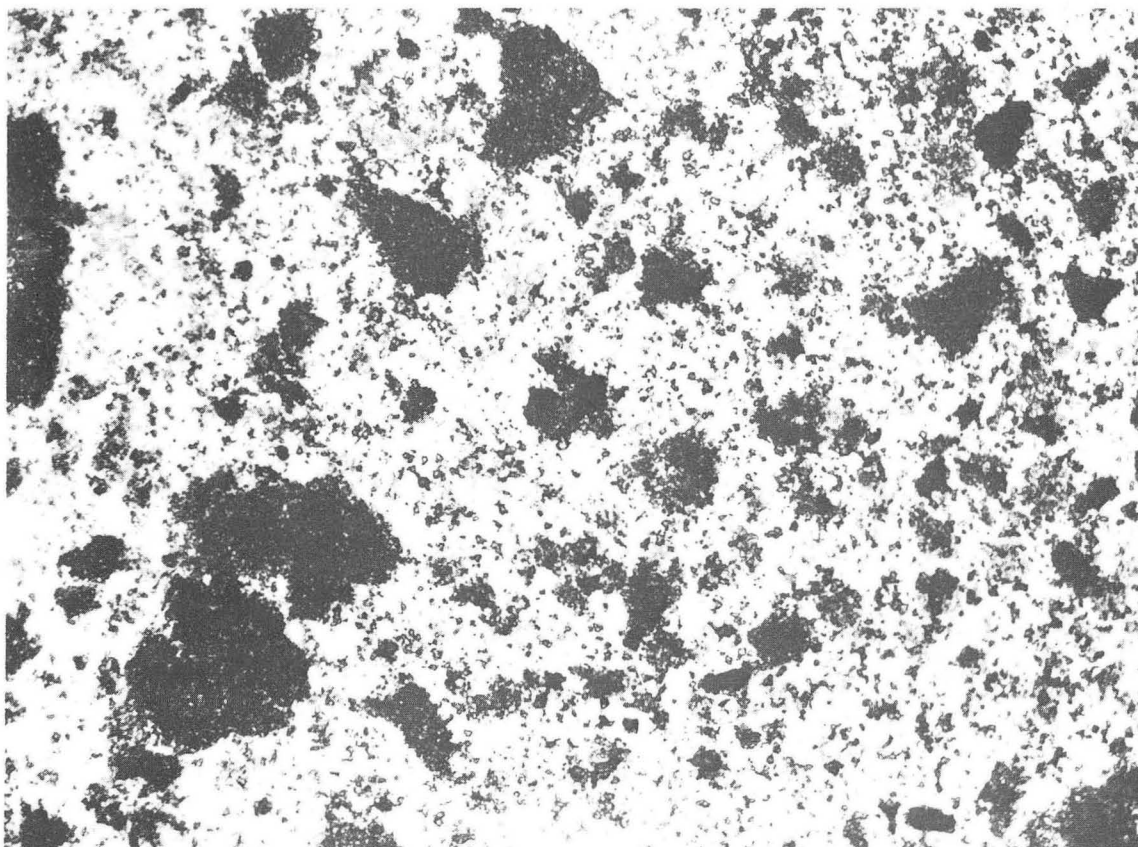
Fig. 12 Photomicrograph of as-pressed
standard PZT. (etched)



20μ

XBB 683-1196

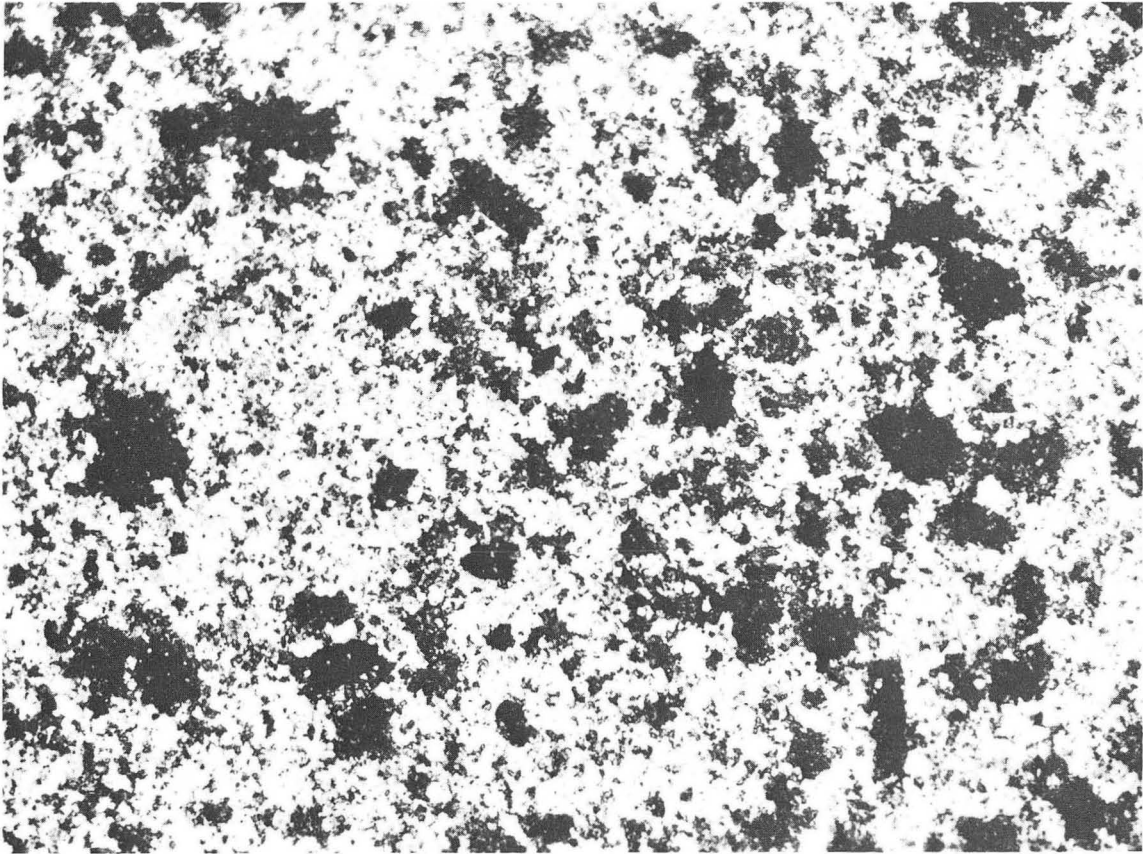
Fig. 13 Photomicrograph of as-pressed
 Bi_2O_3 doped PZT. (etched)



20 μ

XBB 683-1198

Fig. 14 Photomicrograph of as-pressed
 Al_2O_3 doped PZT. (etched)



20μ

XBB 683-1199

Fig. 15 Photomicrograph of as-pressed
 $\text{Bi}_2\text{O}_3\text{-Al}_2\text{O}_3$ doped PZT. (etched)

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