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Isothermal grain growth and ferroelectric behavior of a fully dense lanthanum doped lead zirconate-lead titanate ceramic

Richard A. Langman
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ISOTHERMAL GRAIN GROWTH AND FERROELECTRIC

BEHAVIOR OF A FULLY DENSE LANTHANUM DOPED

LEAD ZIRCONATE-LEAD TITANATE CERAMIC

by

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CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment
of the requirements for the degree of Master of Science.

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ABSTRACT

Theoretically dense PLZT ($Pb_{.93}La_{.07}(Zr_{.65}, Ti_{.35})_{.9825}O_3$) specimens with average grain diameters of $\approx 1\,\mu m$ were fabricated by a pressure-sintering technique. Specimens were characterized with respect to their electrical and electromechanical properties. The fully dense, single-phase specimens were isothermally heat treated in the temperature range of $1100°C - 1250°C$ for various times in a low activity (PbO) atmosphere to observe isothermal grain growth kinetics and ferroelectric property variation.

The isothermal grain growth of PLZT specimens (in the presence of the low activity atmosphere) obeys the $D^3 - D_o^3 = k't$, relationship with a phenomenological activation energy of 86 K cal./ mole. A solid solution (impurity) drag mechanism is proposed as the controlling grain growth rate mechanism.

Most dielectric and ferroelectric properties were observed not to be a function of the average grain diameter in the range $1-5\,\mu m$. However, the heat treated specimens displayed a 20% increase in the planar coupling factor compared to the pressure-sintered specimen values. This is thought to be due to the introduction of point defects within the single-phase PLZT specimen.

I. INTRODUCTION

A number of interesting properties of ferroelectric ceramics in the solid solution system lead zirconate-lead titanate (PZT) have been recognized and studied for several years. The majority of the available literature (1-13) concerns itself with PZT compositions prepared by conventional sintering techniques and modified by various additions to the solid solution.

Only in recent years have investigators (14-17) concerned themselves with the properties of pressure-sintered compositions in the PZT solid solution system. Extensive studies conducted by Haertling and co-workers (18-22) on pressure-sintered PZT ceramics containing bismuth eventually led to the development of an electro-optic polycrystalline ceramic. Presently investigations by Haertling and co-workers (23-24) have been concerned with the development of an improved electro-optic material, this being a lanthanum modified lead zirconate-lead titanate (PLZT) ceramic. These modified PZT materials developed by Haertling and co-workers at Sandia Corporation exhibit electrically variable coefficients of piezoelectricity and birefringence, as well as a high degree of optical transparency in thin polished plates. Consequently, these ferroelectric ceramics are of particular interest for a variety of electro-optic device applications (22, 25-28).

The performance of the electro-optic devices depends to a considerable extent on the properties inherent to the ferroelectric

ceramic. Thus, one approach for achieving improved electro-optic devices is to fabricate the ceramic with precisely controlled ferroelectric and optical properties. The optimization of these properties can be achieved by carefully controlling the following: (1) chemical composition, (2) chemical homogeneity, (3) micro-structure and (4) density (near theoretical).

The variation of the piezoelectric and ferroelectric properties of a polycrystalline material relative to its microstructure has been investigated to some extent (12, 20, 29-31). More specifi-cally the relevant aspects of microstructure studied have been size and distribution of the grains and pores, and phase constitution. These investigations have shown that properties can be considerably altered by the variation of these microstructural parameters. Therefore, microstructural development is important if controlled and reproducible piezoelectric and ferroelectric properties are to be realized.

The present study was undertaken with the purpose of examining the influence of certain microstructual features on the electrical and electromechanical properties of PLZT ferroelectric ceramics. The text will present the results obtained for a fine-grained ($\approx 1 \mu m$) pressure-sintered PLZT composition, which was isothermally heat treated in an effort to obtain specimens with a controlled microstructual variation. The nominal composition selected for this study contained seven atom percent lanthanum and a 65/35

atom ratio of Zr/Ti (designated 7/65/35)*.

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*This composition is discussed in references (23, 24).

II. EXPERIMENTAL PROCEDURE

1. Material Preparation

A 500 gram lanthanum doped lead zirconate-lead titanate composition was compounded from the appropriate oxides* in accordance with the following chemical formula

$$Pb_{.93} La_{.07} (Zr_{.65}, Ti_{.35})_{.9825} O_3 \tag{1}$$
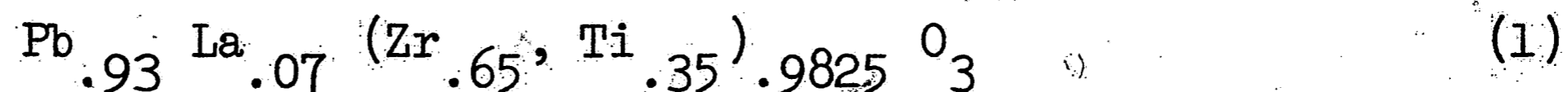
The basic powder preparation procedure was a modified version of the technique employed by Haertling (24). Dry oxides of PbO, TiO_2 and ZrO_2 were weighted to the nearest 0.1 gram. La_2O_3 was weighted hot to the nearest 0.1 gram following a heat treatment** at 900°C for 1.5 hours in a clean Pt crucible in order to insure complete removal of any moisture present. The oxides were then transferred to a one quart polyethylene jar mill containing high density alumina grinding media and milled for 1 hour in a minimum amount of distilled water. The slurry was then poured into a Buchner funnel containing a filter*** paper, and a mechanical vacuum pump was utilized to remove the water.

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* U.H.P. PbO, Electronic grade, Hammond Lead Products, Inc., Hammond, Indiana; ZrO_2 C. P. Grade, Tizon Chemical Company, Flemington, New Jersey; TiO_2 Type 2650, Whittaker, Clark and Daniels, Inc., New York, New York; La_2O_3, City Chemical Corporation, New York, New York.

** Heat treatment temperature was determined by a preliminary thermogravimetric analysis.

*** No. 42 Whatman Filter Paper, W & R Balston Limited, England.

The resultant filter cake was then transferred to a teflon bowl and dried at 110°C for several hours. The dried filter cake was then crushed in a teflon bowl with a teflon pestle and passed through a 65 mesh sieve prior to calcining at 900°C for 1 hour in a covered alumina crucible. The reacted material was then placed in a polyethylene jar mill containing high density alumina grinding media and milled for 1 hour in a minimum amount of acetone. This slurry was then poured into a Buchner funnel containing a filter paper, and a mechanical vacuum pump was utilized to remove the acetone. The filter cake was then transferred to a teflon bowl and dried at 110°C for several hours. The dried filter cake was then crushed in a teflon bowl with a teflon pestle and passed through a 65 mesh sieve prior to heat treating at 700°C for 30 minutes in a covered alumina crucible. This heat treatment was employed to remove any residual acetone which would result in a chemical reduction of the PLZT slug upon pressure-sintering. The heat treated powder was then forced through a 400 mesh nylon sieve using a teflon pestle.

2. Powder Characterization

Quantitative chemical analysis determinations for the four major elemental components of the calcined PLZT powder are reported in Table I in weight percent oxide. A duplicate analysis was also performed in order to ascertain the relative accuracy of the chemical analysis. The determination of lanthanum by this

TABLE I

WET CHEMICAL ANALYSIS* AND X-RAY SPECTROCHEMICAL**

ANALYSIS OF CALCINED PLZT POWDER

Oxide	Theoretical Composition Wt. %	Wet Chemical		X-Ray Spectrochemical Wt. %
		1st analysis Wt. %	2nd analysis Wt. %	
La_2O_3	3.51	4.00	3.71	3.22
PbO	63.84	63.74	64.30	66.11
ZrO_2	24.20	23.73	23.64	22.81
TiO_2	8.45	8.44	8.41	7.86

*   National Spectrographic Laboratories, Inc.,
    19500 South Miles Road, Cleveland, Ohio

** Ms. S. M. Vincent, Bell Laboratories
    Murray Hill, New Jersey

TABLE II

SPECTROGRAPHIC ANALYSIS* OF CALCINED PLZT POWDER

Element	Weight Percent Oxide
Al	0.051
Si	0.044
Ca	0.013
K	0.005
Fe	0.003
Mg	0.003
Ag	<0.001
Cu	<0.001
Mn	<0.001
Ba	<0.001
Na	<0.001

* National Spectrographic Laboratories, Inc., 19500 South Miles Road, Cleveland, Ohio

technique, as indicated in Table I, displays the greatest degree
of variation, while zirconium, lead, and titanium determinations
were shown to be more repeatable. X-ray spectrochemical analysis,
as reported in Table I, was utilized in order to further characterize
the chemical composition of the calcined powder. In the opinion
of the analyst the values determined for lead and zirconium by
this technique are susceptible to the greatest degree of error.

Spectrographic analysis for the determination of the impurities
present in the calcined powder are given in Table II. Based upon
raw material specifications the two major impurities (Al_2O_3 and
SiO_2) present are attributable to the zirconium dioxide. The two
milling operations employing high alumina grinding media also
contribute to the Al_2O_3 impurity level detected.

3. Sample Fabrication

Specimens were dry-pressed at 3000 psi into a slug 0.875
inches in diameter and approximately 1.1 inches high. The
specimen slug was then placed in the vacuum hot-press* assembly
(Figure 1) and the chamber was pumped down to approximately
1×10^{-5} torr for the 24 hours prior to the pressure-sintering of
the slug. Just prior to the actual pressure-sintering of the slug
the chamber was backfilled to a pressure of approximately 19.7 psi

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* Vacuum Hot-Press Sintering Furnace, Series 3600, Model 1-2300,
  Vacuum Industries, Inc., Somerville, Massachusetts.

FIGURE 1
HOT-PRESS DIE ASSEMBLY

LEGEND

1. UPPER ALUMINA PLUNGER
2. FUSED - SILICA INSULATION SLEEVE
3. INDUCTION COIL
4. > 60 MESH ZIRCONIA PACKING POWDER
5. PLZT SLUG
6. ZIRCONIA - FELT INSULATION LINING
7. ALUMINA DIE SLEEVE
8. CASTABLE CERAMIC INSULATION
9. SILICON CARBIDE SLEEVE
10. HASTELLOY X SUSCEPTOR
11. Pt TO Pt-13% Rh THERMOCOUPLE
12. THERMOCOUPLE LEADS
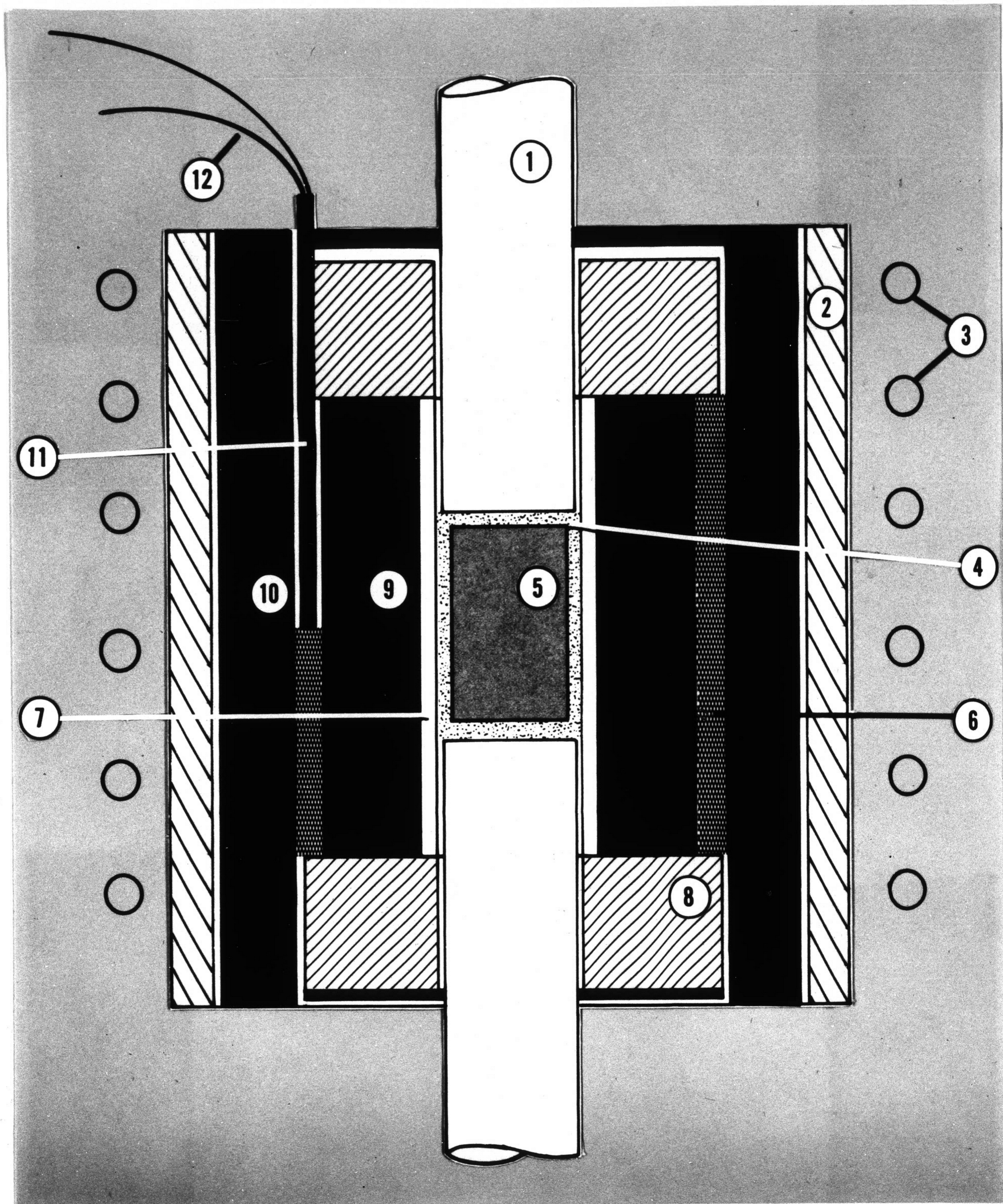
with a gas mixture consisting of 80% He - 20% O_2. The Hastelloy X
susceptor was then inductively heated at the average rate of 540°C
per hour. A pressure of 6000 psi was applied to the slug 30 minutes
after temperature stabilization was achieved at 1075°C. The slugs
were pressure-sintered for a total of 16 hours with the pressure
being maintained at 6000 ± 200 psi during the first 5 hours and
6000 ± 500 psi during the remaining time. At the end of the 16 hour
period the pressure was removed while the sample was at temperature
and the R. F. power to the susceptor was gradually reduced over a
1 hour period. The pressure-sintering conditions used, i.e., time,
temperature, pressure, atmosphere, and sample size were determined
by a preliminary study to yield slugs of maximum bulk density con-
sistent with a fine grain size. Upon removal of the slug from the
hot-press assembly its bulk density was determined using the
Archimedes' liquid displacement technique. The slug was then
machined* to a diameter of 0.500 inches and sliced to produce disks
0.030 inches thick.

4. <u>Isothermal Heat Treatment</u>

Two disks from each pressure-sintered slug were retained in
order to characterize the initial properties of a given slug. These
disks were selected such that one disk came from the center of the
slug, while the other originated at the end of the slug. Also,
one disk was selected at random and broken into quarters to facili-

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*Insaco Incorporated, P. O. Box 422, Quakertown, Pennsylvania 19851.

tate grain diameter determinations at the various times for a given temperature. Prior to isothermal heat treatment of the PLZT disks, from which electrical property measurements were determined, their weights were carefully determined and recorded.

Closed end Pt tubes approximately 5 inches in length by 0.65 inches in diameter were fabricated and loaded with a two phase mixture consisting of 15 grams of 90 weight % $PbZrO_3$ - 10 weight % ZrO_2 in order to provide a PbO atmosphere of constant activity during the isothermal heat treatment. Each individual disk and an accompanying quarter disk were vertically positioned in the packing powder and then the Pt vessel was welded shut. The Pt vessels containing the PLZT disks of a given slug were then placed in a Pt wound tube furnace and heated up to the appropriate temperature of interest at the rate of $200°C$ per hour. Pt vessels containing disks which were heat treated for relatively short periods of time (< 8 hours) were positioned in the hot zone of the tube furnace while the furnace was at the temperature of interest. In all instances the Pt vessels were removed at temperature upon attainment of the desired soak period and then immediately placed in a furnace at $600°C$ and allowed to furnace cool to room temperature. Once at room temperature the samples were removed from the Pt vessel, the packing powder was removed from the disk, and the weight of the heat treated disk determined and recorded.

5. Measurement Techniques

Specimens for grain diameter determinations were mechanically polished on 600 grit SiC paper and then on a Syntron bowl containing a slurry of 0.3 μm gamma alumina powder. These specimens were then thermally etched for 20 minutes at 1050 $\pm$ 50°C in a covered Pt crucible containing a mixture of 90 weight % $PbZrO_3$ - 10 weight % ZrO_2 powder in order to provide a PbO rich atmosphere. Formvar two-stage replicas were then prepared of the thermally etched surface for examination in the electron microscope. Average grain diameter measurements were determined from electron microscope photomicrographs by the linear intercept method as described by Hillard (32). The average equivalent spherical grain diameter was then determined by multiplying the average intercept length by 1.5 as suggested by Fullman (33). The coefficient of variation of the average intercept length was maintained at less than 7 percent by counting a minimum of at least 80 intersections. Wherever possible the accuracy of the technique was improved by counting approximately 200 intersections.

Ferroelectric domain texture was revealed by chemically etching polished specimens with a dilute (5%) solution of HCl in distilled water containing 1 drop of 50% HF per 100 cm^3 of solution. These specimens were then evaporated with gold and examined in a scanning electron microscope.

Electrical property measurements were made on PLZT disks which were electroded by evaporating titanium and then gold on the disks major surfaces. Several days after electroding electrical property measurements were performed on the disks just prior to poling and 24 hours after poling. The disks were poled at room temperature in a freon bath with an applied electric field of 20 kV/cm maintained for 5 minutes.

A capacitance bridge* was utilized for small signal dielectric measurements of capacitance and dissipation factor (tan δ) at 1 kHz. Determinations of the planar coupling factor (k_p) were made by the resonance - antiresonance technique in accordance with the IRE Standards on piezoelectric ceramics (34).

*Type 1673-A Automatic Capacitance Bridge and Type 1672-AS2 Digital Control Unit, General Radio Company, Concord, Massachusetts

III. RESULTS AND DISCUSSION

1. Pressure-Sintered Specimens

Pressure-sintered slugs were reproducibly fabricated with bulk densities of $7.855 \begin{smallmatrix} - & 0.000 \\ + & 0.001 \end{smallmatrix}$ gm/cm^3 and average grain sizes of 1.1 $\pm$ 0.2 μm. The theoretical density for the 7/65/35 composition has been reported by Haertling and Land (23) to be 7.856 gm/cm^3. This indicates the fabrication procedure has yielded slugs with very high relative densities. Average grain size determinations indicated that grain size gradients within a given slug were very small ($\leq$ 0.05 μm).

The microstructural character of a typical pressure-sintered slug is shown in Fig. 2. The electron micrograph of the polished and thermally etched specimen clearly depicts a highly dense material consisting of relatively uniform equiaxed grains. Additional microstructural examination was performed on the surface produced by fracturing a specimen. The scanning electron micrograph, shown in Fig. 3, clearly illustrates the intercrystalline nature of the fracture. The effect of thermally etching the same specimen as described in section II-5 is shown in Fig. 4. The scanning electron micrograph shows the rather rapid rounding of the fractured surface grains to lower the energy configuration. No strong surface energy anistropy effects are in evidence. This rapid transition of the surface grains under thermal etching conditions is thought to be aided by the high vapor transport rate of PbO at the surface of the
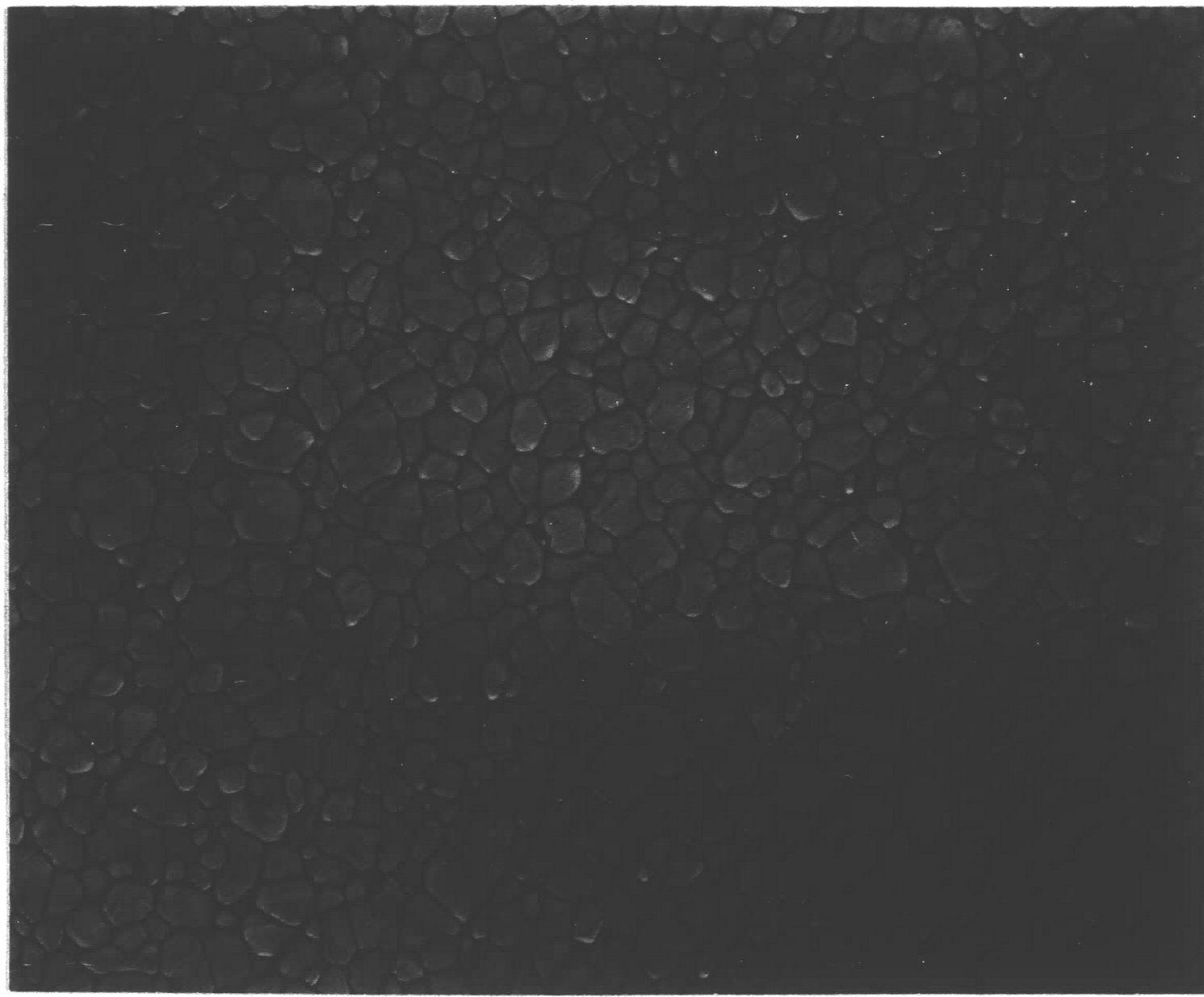
FIGURE 2

ELECTRON MICROGRAPH SHOWING MICROSTRUCTURE OF
PRESSURE-SINTERED PLZT, 1075°C-
16 HRS. - 6,000 PSI, (3,800X)
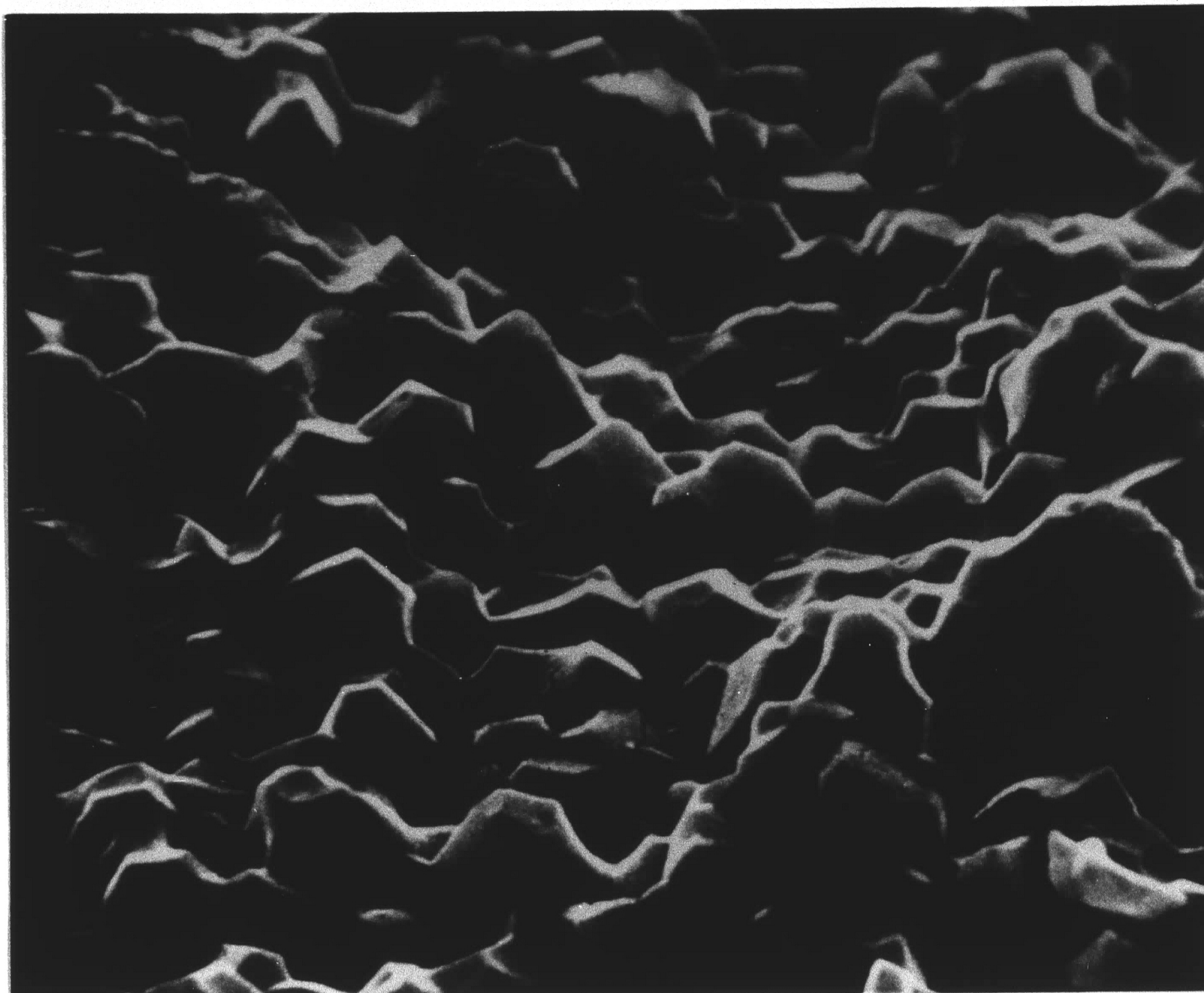
FIGURE 3
SCANNING ELECTRON MICROGRAPH OF A
FRACTURED PLZT SURFACE (10,000X)

FIGURE 4
SCANNING ELECTRON MICROGRAPH OF A FRACTURED PLZT SURFACE
WHICH HAS BEEN THERMALLY ETCHED (10,000X)

specimen. The Zr, Ti, and La ions present at the surface must also move rapidly by volume or surface diffusion which is enhanced by the vapor transport of PbO.

2. Isothermal Heat Treatment

In the temperature region studied (1100°C - 1300°C) the PLZT material contains two species which are quite volatile, these being PbO and O. The mechanism and kinetics of PbO loss in PZT ceramics has been investigated by Northrop (35, 36). Atkin and Fulrath (9) have established that single-phase PZT can exist over a range of stoichiometries by accommodating changes in the concentration of lattice vacancies. However, an equilibrium atmosphere of sufficient PbO activity must be provided in order to maintain the PZT composition in the single-phase field with a constant Zr/Ti ratio. In the present study this was accomplished by the use of the 90 weight % $PbZrO_3$ - 10 weight % ZrO_2 mixture. Such a two phase mixture in a binary system will have a constant activity. According to the data of Atkin and Fulrath (9) the PbO activity will be about 0.05. Since activities decrease upon substitution of Ti for Zr (9) we are assured our 65/35 composition will be within the single-phase field. How near the boundary (saturated with (Zr, Ti) O_2) and what effect 7 atom percent lanthanum substitution will have are unknown.

Lead zirconate - lead titanate possesses the perovskite crystal structure with the Pb ions on the A sites, the corners, the Ti or Zr ions on the B sites, the center, and O ions on the faces of the unit cell. Substantial lattice vacancies may be introduced into the

perovskite structure if the electronuetrality requirement is satisfied. Suggested mechanisms which may operate to satisfy this requirement include an anion vacancy formation at an <u>adjacent</u> lattice site, substitution of an ion on an <u>adjacent</u> site with an incorrect valence, or the localization of electron holes <u>at</u> the vacancy.

In PLZT vacancies are introduced by the random substitution of La^{+3} on Pb^{+2} sites producing (A site) vacancies and probably a smaller fraction of Zr^{+4} amd Ti^{+4} (B site) vacancies. During the heat treatment of the PLZT the formation of Pb and O vacancies occur whose concentrations are controlled by the PbO activity of the system.

As anticipated an activity equilibration process was observed to take place between the two phase ($PbZrO_3$ and ZrO_2) packing powder and the PLZT disk. The PLZT disks in all cases lost weight, presumed to be PbO, as a result of this process. These weight losses as determined from the disks percent weight change were observed to be temperature dependent and are given in Table III. This observed temperature dependence corresponds to an increasing relative difference between the PbO activity of the disk and the packing powder with temperature. The activity equilibration process as monitored by the disks weight change was approximately 60 percent complete within the first half hour and fully complete in less than three hours. Therefore, for the majority of the time at temperature during the heat treatment the samples were at equilibrium.

Haertling and co-workers (23) have similarly observed PbO losses to take place during conventional sintering studies of PLZT in

TABLE III

Effect of Isothermal Heat Treatment Temperature On

The Percent Weight Change Resulting From PbO Activity Equilibration

Temperature °C	Range of Heat Treating Times (Minutes)	Percent Weight Change
1100	480 - 11,820	- 1.16 ± 0.21
1150	480 - 6,500	- 1.64 ± 0.04
1200	180 - 6,120	- 1.79 ± 0.17
1250	180 - 1,920	- 2.48 ± 0.07
1300	480 - 1,920	- 4.89 ± 0.49

a PbO rich atmosphere. The investigation utilized samples based on
the same formula composition used in the present study (see eq. 2)
and an alternate formula composition (see eq. 3) commonly used for
PZT preparation with three-valent dopants such as lanthanum.

$$Pb_{1-x}La_x(Zr_y, Ti_z)_{1-\frac{x}{4}} (\square_B)_{\frac{x}{4}} O_3 \qquad (2)$$

$$Pb_{1-\frac{3x}{2}} (\square_A)_{\frac{x}{2}} La_x(Zr_y, Ti_z)O_3 \qquad (3)$$
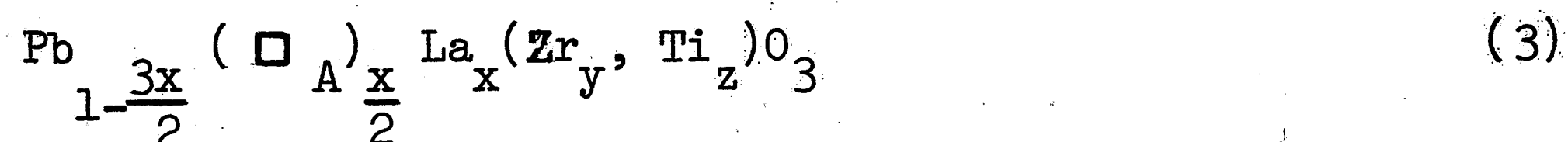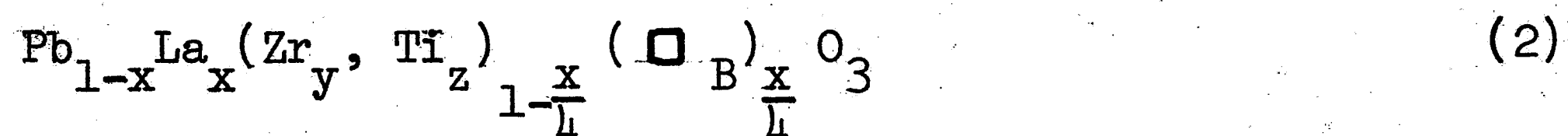
Specimens whose composition were based on equation 2 consistently
lost PbO to the atmosphere, while those based on equation 3 con-
sistently gained PbO. Since Haertling does not provide the exact
experimental details, i.e., activity of the PbO atmosphere, com-
position studied, and sintering temperature, a precise comparison
with the present study can not be made. However, the present study
does indicate that equation 2 is probably PbO rich with respect to
the activity given by the $PbZrO_3$ - ZrO_2 packing powder.

The samples which experienced weight losses of less than
approximately 2.6 weight percent (see Table III) retained their
characteristic yellow appearance and were transparent to light in
thin polished plates. Examination of the polished disks by means
of the light microscope did not reveal the presence of a second
phase. Therefore, these disks were still considered to be in the
single-phase field, but of modified stoichiometry depending upon
their weight losses.

PLZT specimens which experienced weight losses in excess of
2.6 weight percent were brownish in appearance, as opposed to their
initial yellow appearance. Optical microscopy as performed on these
polished specimens revealed the presence of an apparent second phase
(see Fig. 5) and also the introduction of a considerable amount of
porosity.

The precipitation of a second phase in PZT ceramics has been
explained (12, 37) on the basis that excessive PbO losses produce
a shift in the Zr/Ti atom ratio. Therefore, PbO losses which can
not be fully accomodated by lattice vacancies results in a composi-
tional shift towards a material of a lower zirconium atom ratio
and the subsequent precipitation of ZrO_2 as a second phase. This
process is consistent with the activity composition relationship
displayed by the data of reference 9.

Weight losses in excess of 2.6 weight percent (values as high
as 5.6 weight percent were observed) were observed to occur under
the following heat treating conditions (1) greater than 180-480
minutes at 1300°C (2) greater than 1950 minutes at 1250°C and (3)
greater than 6120 minutes at 1200°C. The observed weight losses
under the conditions cited did not vary in any consistent manner
with time or temperature. Although the exact mechanism producing
these excessive weight losses was not investigated, possible expla-
nations are: (1) diffusion of PbO into the Pt vessel and (2) poor
sealing of the Pt vessel allowing PbO vapor to escape. In any

FIGURE 5

OPTICAL MICROGRAPH OF A POLISHED PLZT SPECIMEN (1300°C-480 MINUTES)
SHOWING THE PRESENCE OF A SECOND PHASE AND POROSITY (500X)

event these two-phase samples were excluded from consideration in the grain growth study reported next.

3. Isothermal Grain Growth

Virtually no information is available in the literature concerning the isothermal grain growth of fully dense PZT or modified PZT ceramic systems. Generally the previous grain growth studies (9, 18) have been conducted with a varying degree of complication due to the simultaneous densification process, chemical homogenization and the presence of porosity. In the present study an attempt was made to eliminate these variables and investigate the isothermal grain growth kinetics of a fully dense fine-grained lanthanum modified PZT ceramic.

During heat treatment at elevated temperatures of a fine-grained polycrystalline material an increase in the average grain diameter is observed. This increase in grain diameter results from the decrease in energy achieved by means of decreasing the grain boundary area and thus the total boundary energy of the sample.

When the grain boundary mobility is the controlling parameter for grain growth, the rate should be inversely proportional to the average radius of curvature of the boundary (38, 39). This boundary curvature is then taken to be inversely proportional to the average grain diameter. Thus, equation 4 gives the grain diameter-time

relationship obtained for the situation where the boundary mobility is rate controlling.

$$D^2 - D_o^2 = kt \qquad (4)$$

The instantaneous average grain diameter is given by D and it is equal to D_o when the time equals zero. The grain growth rate constant k depends upon the temperature and the mobility of the boundary.

It has been commonly observed that the mobility of the grain boundary can be drastically altered such that the grain growth rate becomes proportional to the cube root of time (40-42). Brook (43) has summarized the particular processes which produce the cubic relationship as follows: (a) coalescence of a second phase (44) by lattice diffusion (45), (b) coalescence of the grains in the presence of a liquid phase by a solution - precipitation mechanism (46), (c) boundary migration impeded by a solid solution (impurity) drag mechanism (47) and (d) pore drag mechanisms. The equation describing the grain growth relation for these rate controlling mechanisms is given in equation 5.

$$D^3 - D_o^3 = k't \qquad (5)$$

As pointed out previously the experimental data utilized in order to ascertain the controlling grain growth relation (see eq. 4 and 5) was obtained from specimens which were still single-phase and hence had weight losses of 2.6 weight percent or less. The grain

growth rate observed in these specimens was also considered to be independent of any Pb or O activity variations (9).

The best fit to the isothermal grain growth data, as shown in Fig. 6, was obtained with equation 5 rather than equation 4. A period of incubation or induction for grain growth is suggested in Fig. 6 at the lowest temeprature and shortest time, therefore, this data point was not considered in the determination of the least-squares line. Grain growth rate constants and correlation coefficients resulting from a least-squares fit, for each temperature studied, are presented in Table IV. The correlation coefficients obtained from fitting the quadratic relation (equation 4) to the data were also determined and are given in Table IV. In all instances the best fit to the isothermal grain growth data, as indicated by the higher correlation coefficients, occurred with equation 5.

A phenomenological "activiation energy," as determined by a least-squares analysis of the grain growth rate constants (k') given in Table IV, was 86 K cal./mole. An Arrhenius type plot of the grain growth rate versus the reciprocal of the absolute tempera-ture is given in Fig. 7.

The observation of the $t^{1/3}$ dependence of the average grain diameter in the present study is thought to be due to a solid solution (impurity) drag mechanism as proposed by Brook (47). The
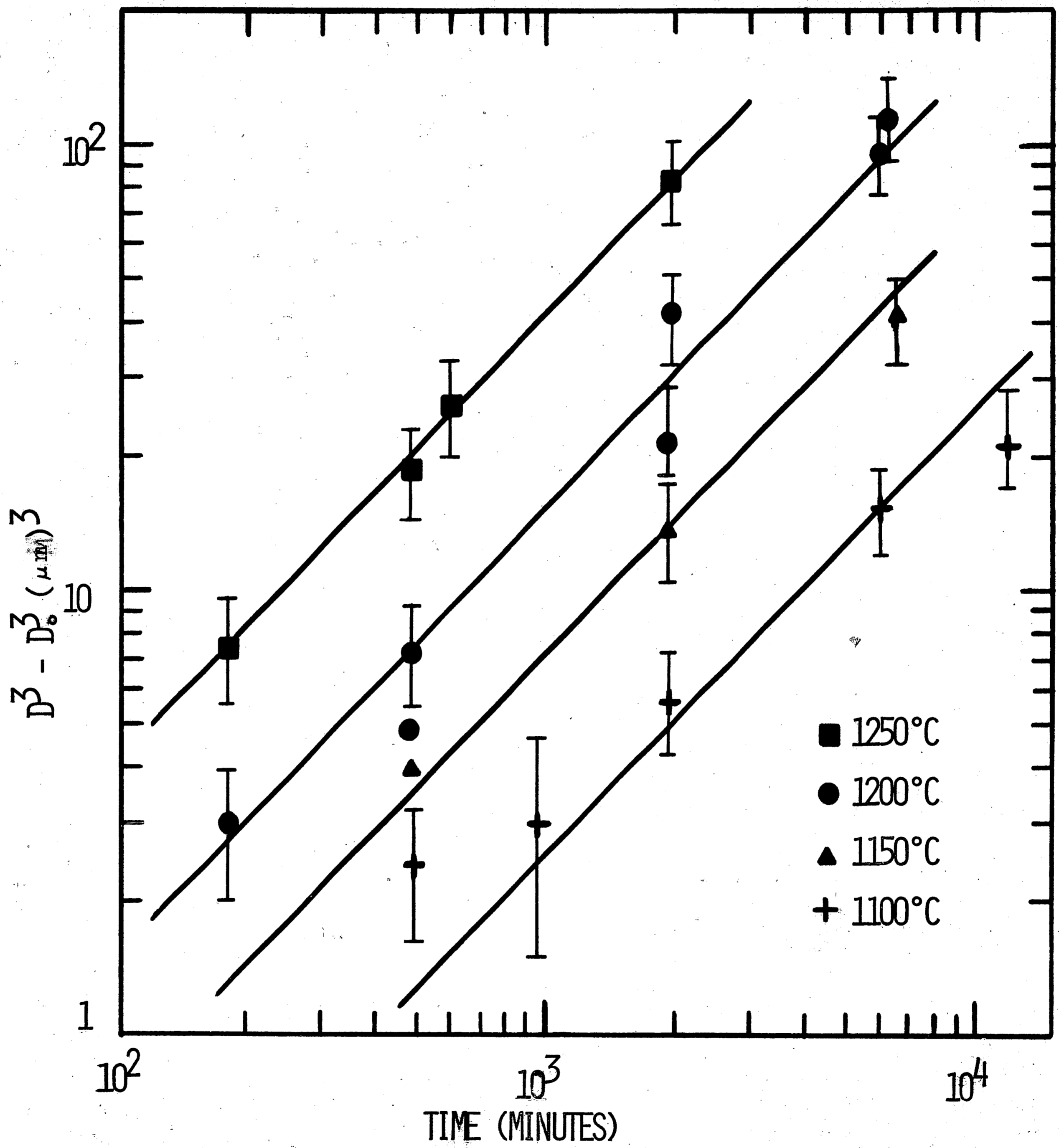
FIGURE 6

LEAST-SQUARES PLOT OF LOG ($D^3 - D_0^3$) VERSUS LOG TIME

TABLE IV

RESULTS OF LEAST-SQUARES ANALYSIS FOR
GRAIN DIAMETER CUBED VERSUS TIME

Temperature °C	k' cm^3/sec	Correlation Coefficient*
1100	3.25×10^{-17}	0.9907
1150	1.04×10^{-16}	0.9992
1200	2.94×10^{-16}	0.9893
1250	7.16×10^{-16}	0.9989

*Correlation coefficients determined for grain diameter squared versus time from 1100°C to 1250°C respectively were 0.9669, 0.9866, 0.9853, and 0.9886.
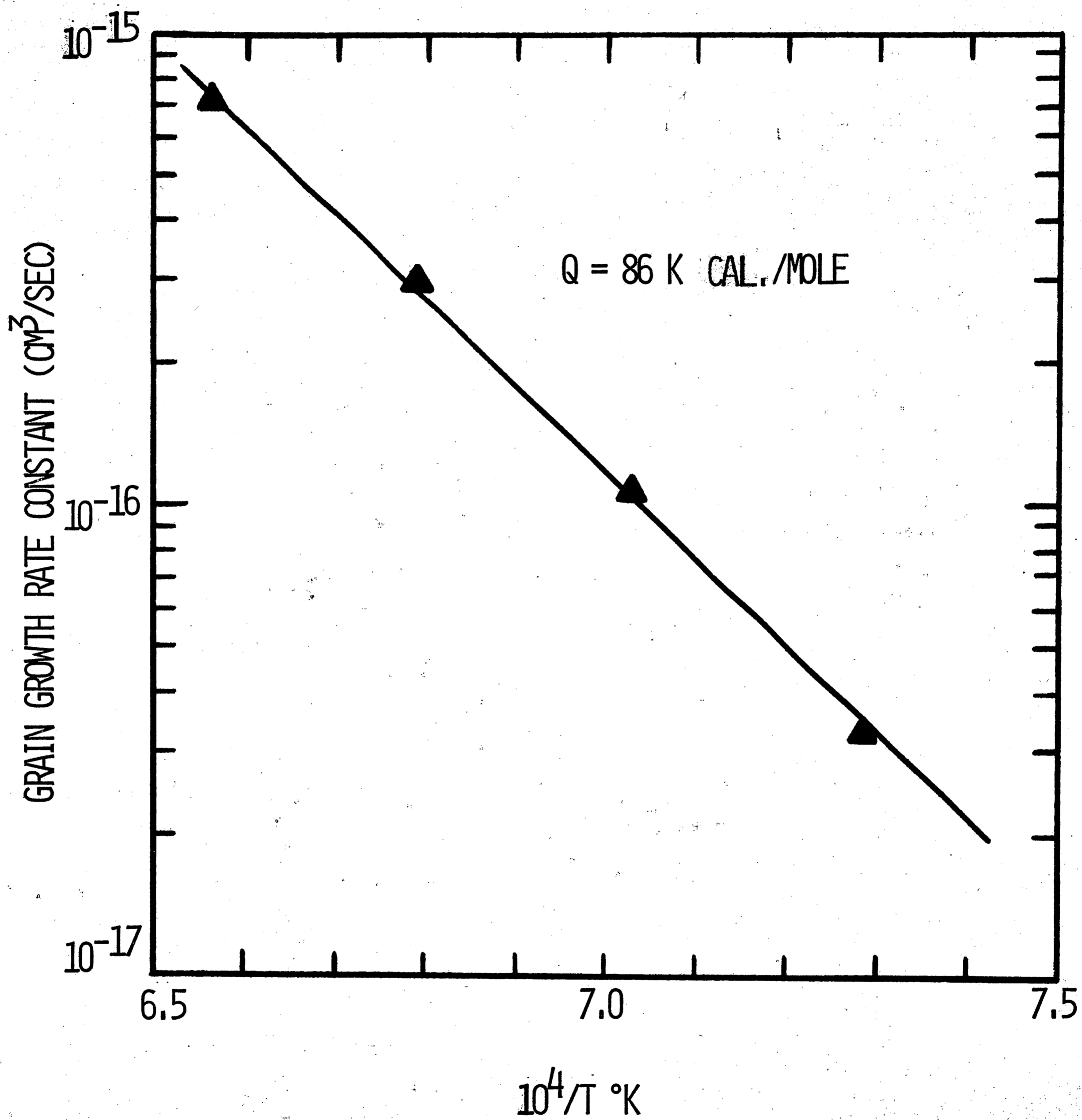
FIGURE 7

ARRHENIUS PLOT OF GRAIN GROWTH RATE VERSUS THE RECIPROCAL OF THE
ABSOLUTE TEMPERATURE

other possible mechanisms as previously discussed were discounted
based upon the following: (a) the presence of a second phase was
not detected, (b) equilibration with the low activity atmosphere
occurred over a relatively short period of time and upon attainment
of this equilibrium condition, a Pb rich liquid should not be
present, and (c) essentially fully dense PLZT specimens were
utilized in this study.

The process by which a solid solution (impurity) drag mech-
anism becomes operative in PZT systems may be related to the presence
of doping ions (9). The introduction of doping ions could result
in the formation of charged vacancies which may be attracted to the
grain boundaries, thereby producing an excess concentration of
doping ions near the grain boundary. Therefore, these adsorbed
ions may serve as an impurity "atmosphere" which results in a sub-
stantial reduction in the grain boundary mobility.

Similar grain growth inhibition has been observed by Haertling
(18) in a 2 atom percent bismuth (Bi^{+3}) doped PZT (65/35 atom ratio
of Zr/Ti) system. The data was obtained under pressure-sintering
conditions and thus is the most comparable study to the present
one available in the literature. Although a $t^{1/3}$ dependence for
grain growth was observed by Haertling the influence of the densi-
fication process, chemical homogenization, and porosity of the
specimens from which the data was ascertained renders any interpreta-

tion questionable, particularly for short times and low temperatures. However, the data obtained at higher temperatures and longer times, where the above mentioned variables have probably been eliminated, does fit the cubic grain growth relationship and thus supports the solid solution (impurity) drag mechanism as proposed in the present study. Also, it is interesting to note that Haertling obtained a phenomenological activation energy of 95 K cal./mole for grain growth which is in reasonable agreement with the value (86 K cal./mole) determined in the present study.

Grain growth data obtained for heat treated specimens which experienced excessive PbO losses (>2.6 weight percent) were found to have grain sizes greater than what would be predicted by using the relation given in equation 5. A typical example would be a specimen which was heat treated for 11,400 minutes at 1200°C with a 3.53% weight loss. The specimen was determined to have a grain size of 8.2 μm while the predicted value as determined from Fig. 6 would be approximately 5.6 μm. These grain size differences between the experimentally observed values and the predicted values are considerably greater than any differences that might arise due to error in experimental technique. Thus, one is lead to believe that excessive PbO losses can rather drastically alter the grain growth rate of these materials.

Typical electron micrographs of polished and thermally etched specimens in order of ascending grain size are given in Figures 8-15. These micrographs portray the microstructural development
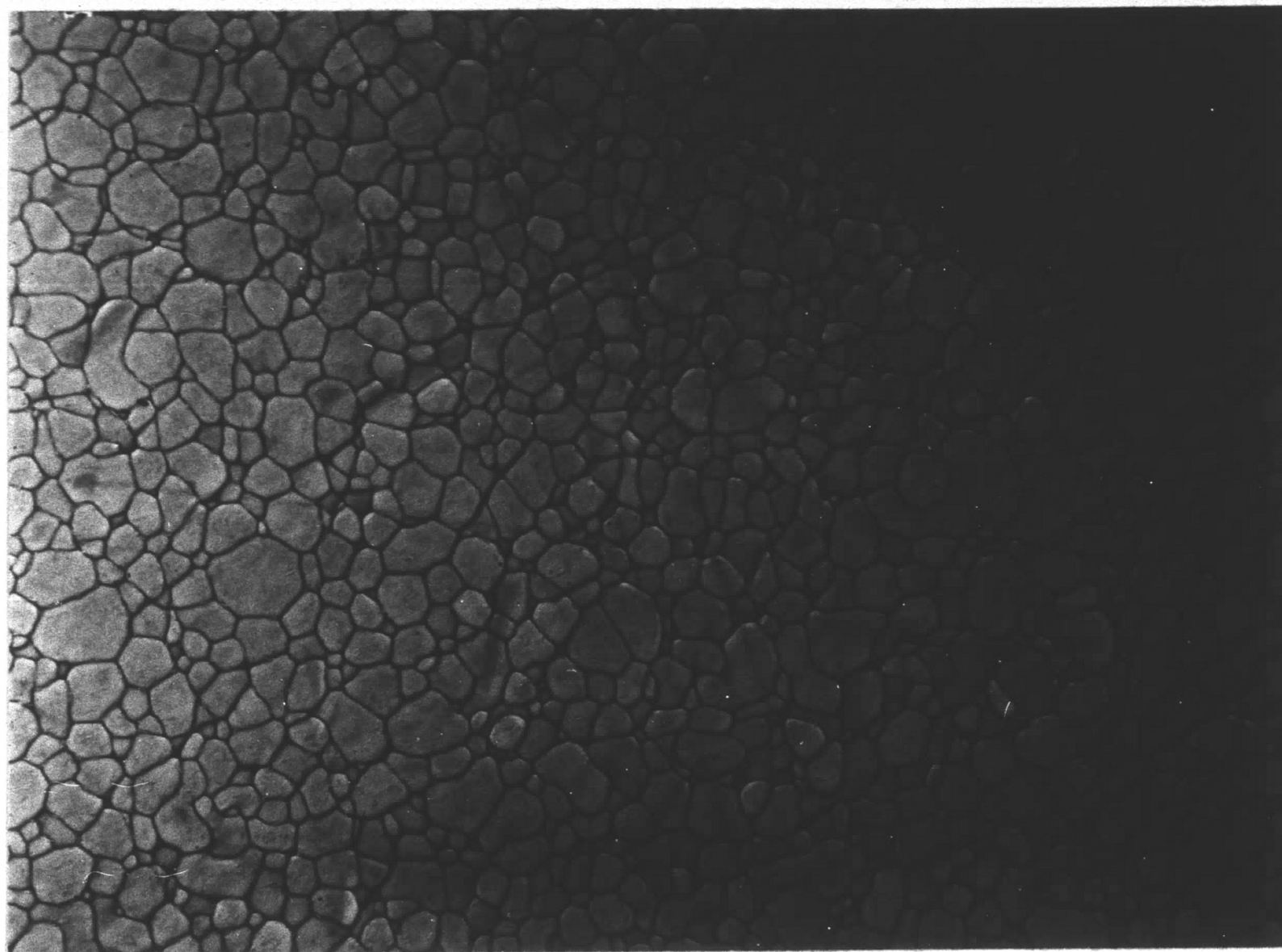
FIGURE 8

ELECTRON MICROGRAPH SHOWING THE MICROSTRUCTURE OF
PRESSURE-SINTERED PLZT (3,800X)
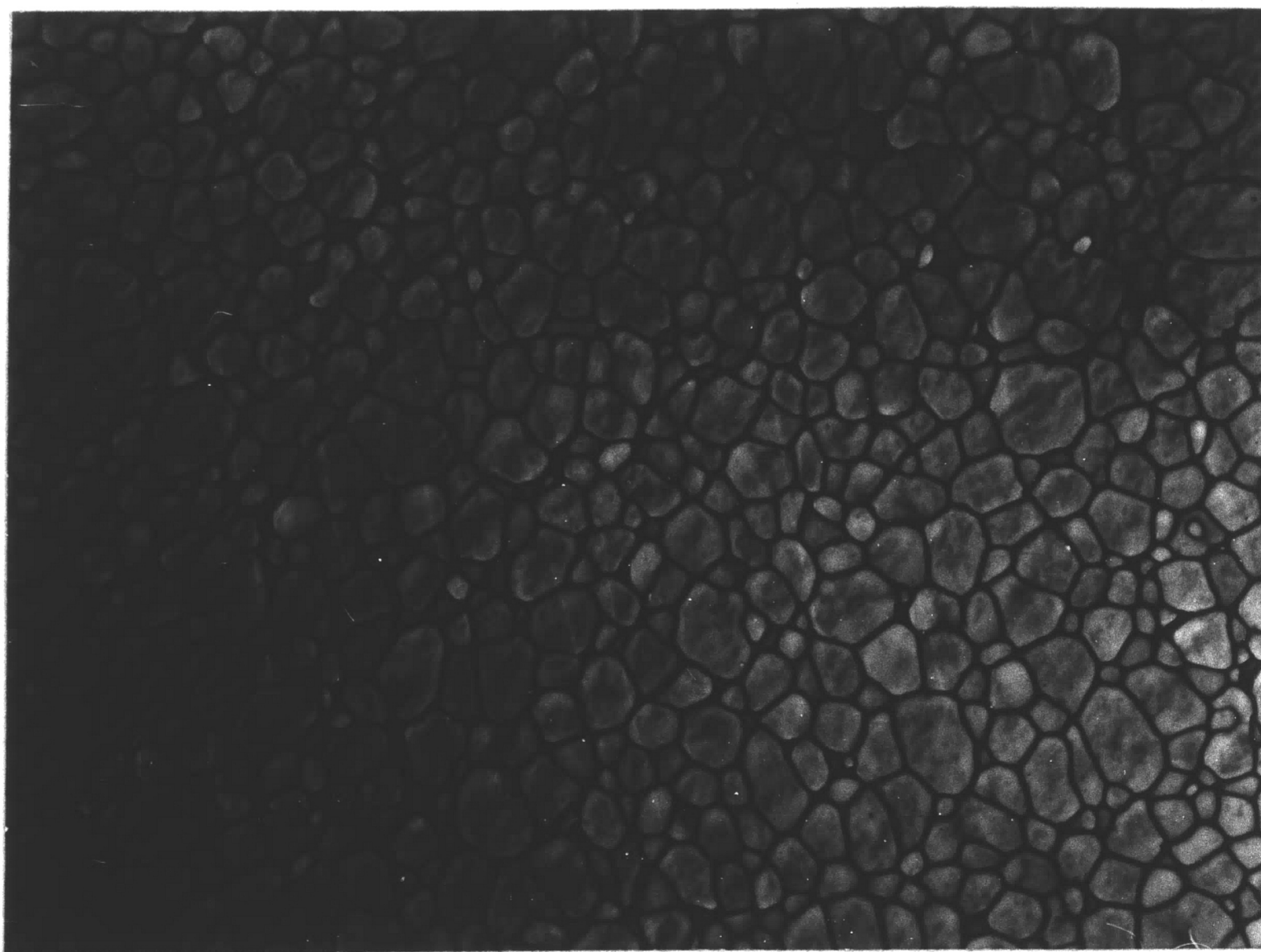
FIGURE 9

ELECTRON MICROGRAPH SHOWING THE MICROSTRUCTURE OF
PRESSURE-SINTERED PLZT (3,800X)
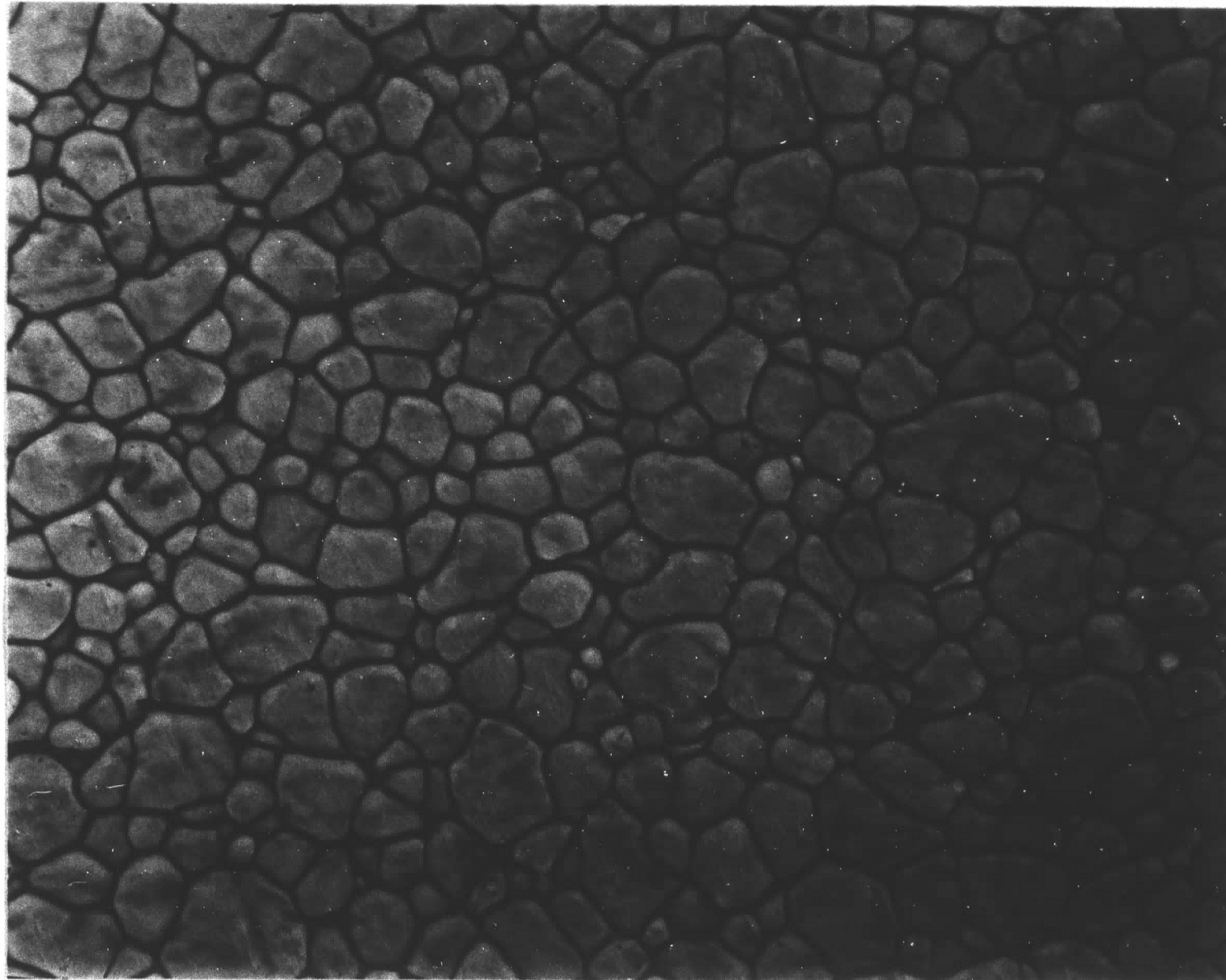
FIGURE 10

ELECTRON MICROGRAPH SHOWING THE MICROSTRUCTURE OF
HEAT TREATED PLZT, 1100°C – 480 MINUTES (3,800X)
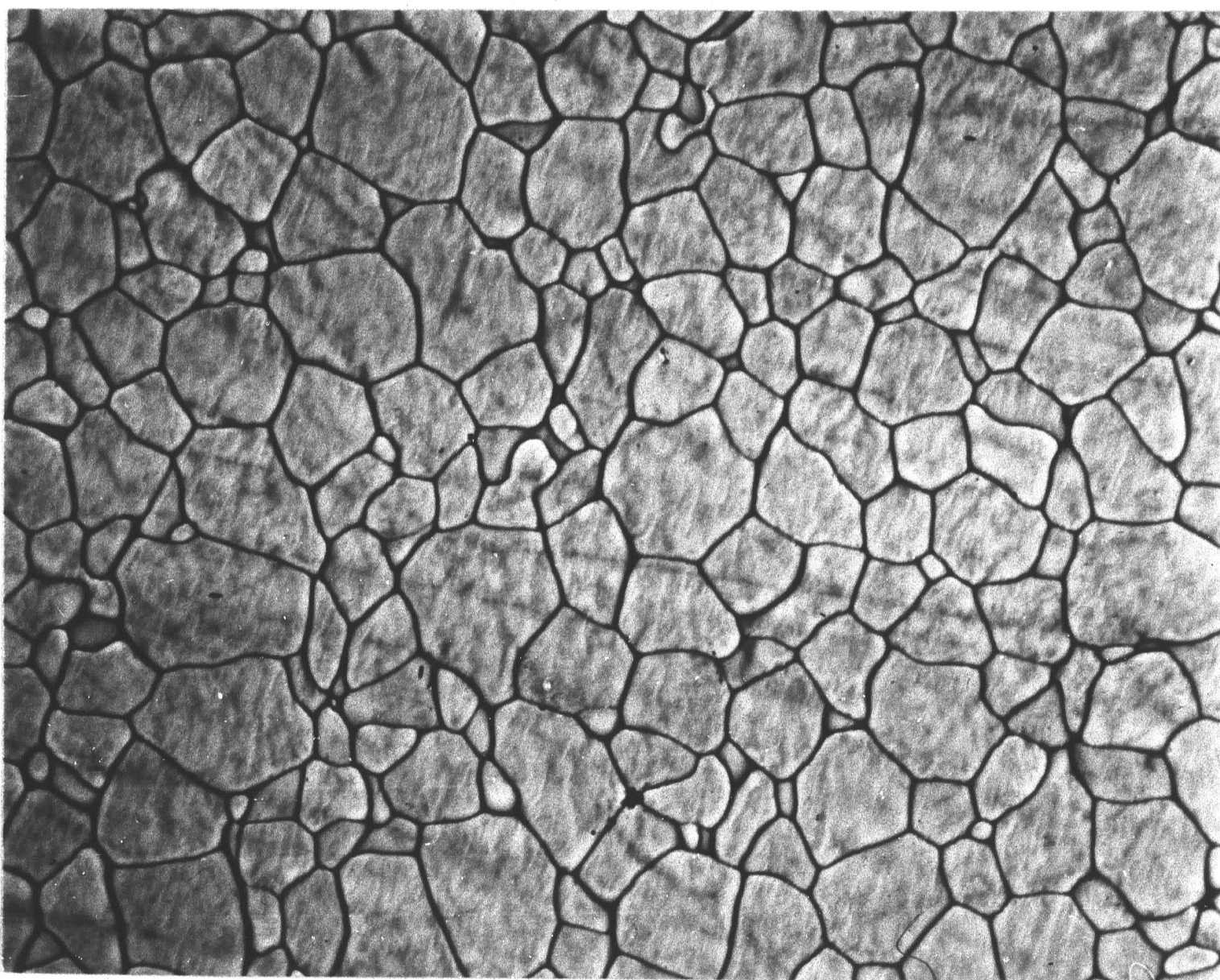
FIGURE 11

ELECTRON MICROGRAPH SHOWING THE MICROSTRUCTURE OF
HEAT TREATED PLZT, 1100°C – 1,920 MINUTES (3,800X)
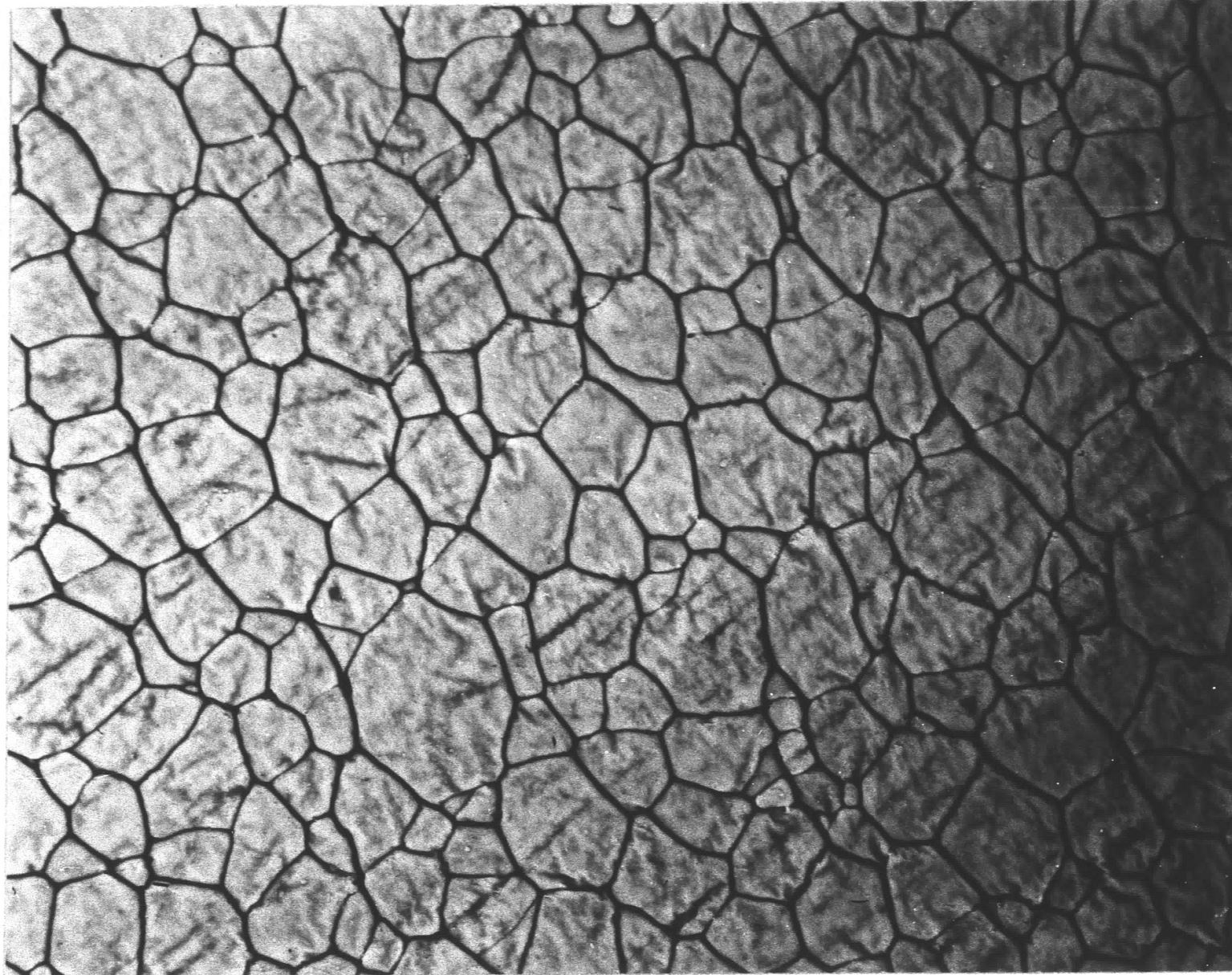
FIGURE 12

ELECTRON MICROGRAPH SHOWING THE MICROSTRUCTURE OF
HEAT TREATED PLZT, 1200°C – 480 MINUTES (3,800X)
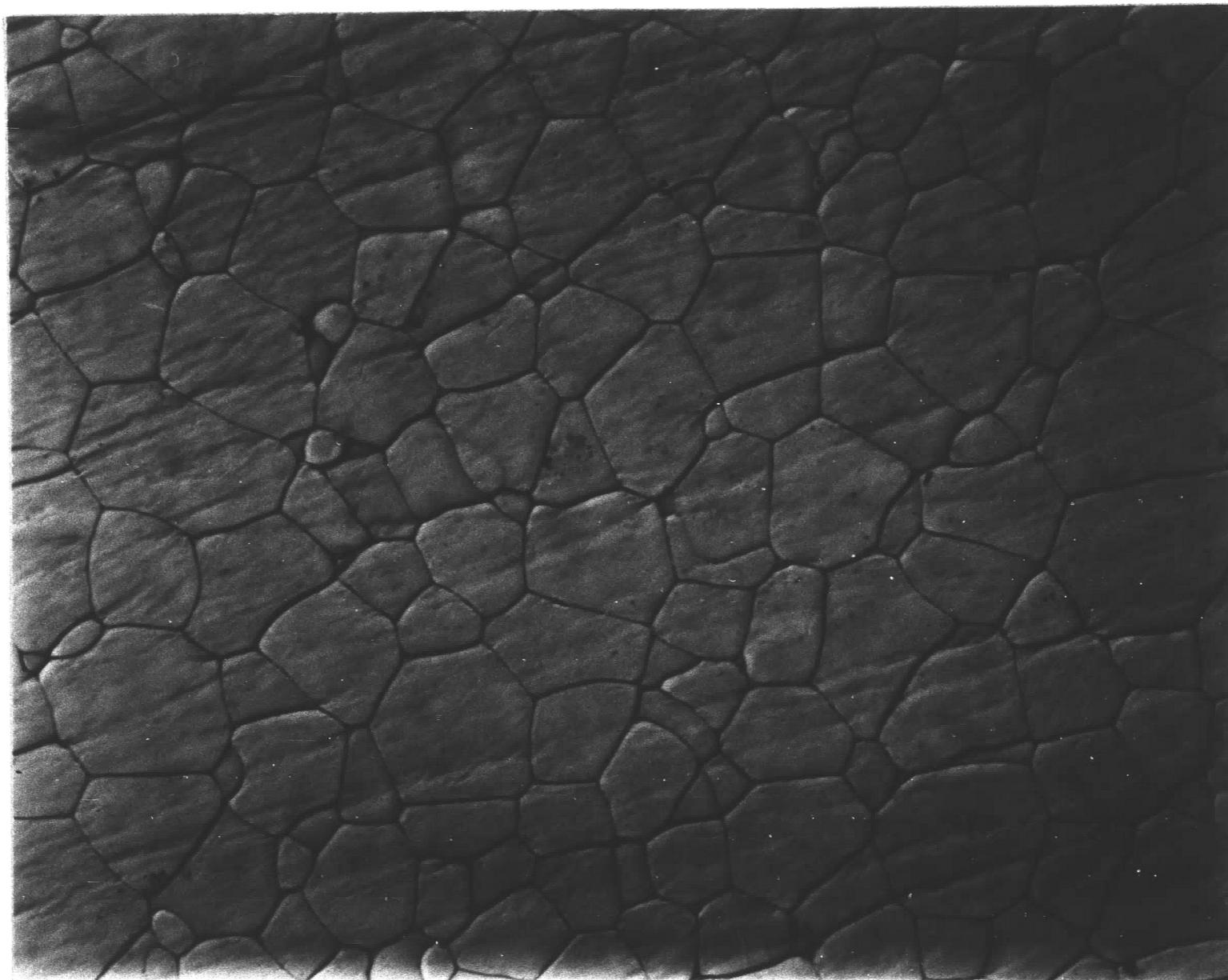
FIGURE 13

ELECTRON MICROGRAPH SHOWING THE MICROSTRUCTURE OF
HEAT TREATED PLZT, 1100°C – 6,000 MINUTES (3,800X)
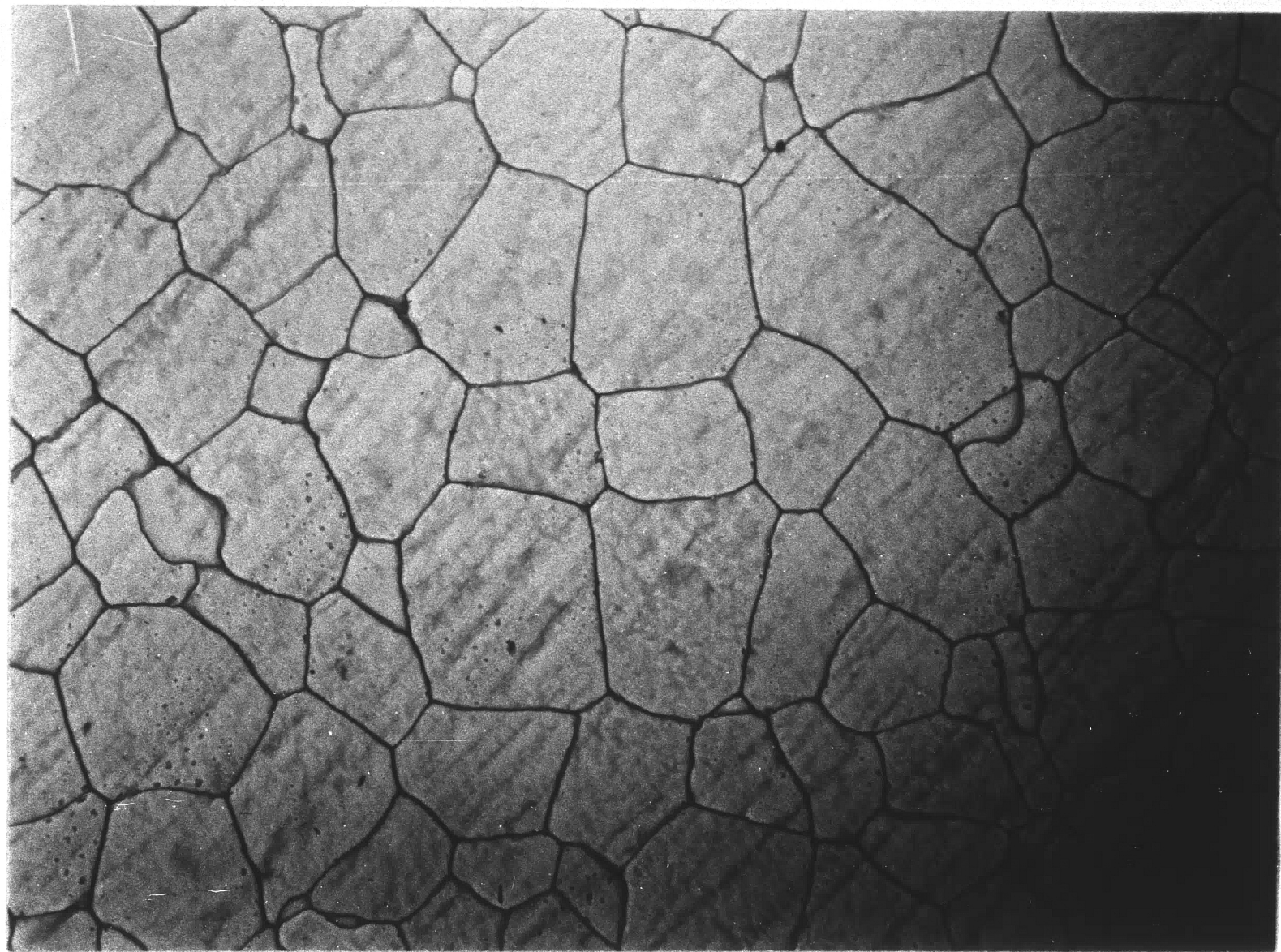
FIGURE 14

ELECTRON MICROGRAPH SHOWING THE MICROSTRUCTURE OF
HEAT TREATED PLZT, 1200°C - 1,920 MINUTES (3,800X)
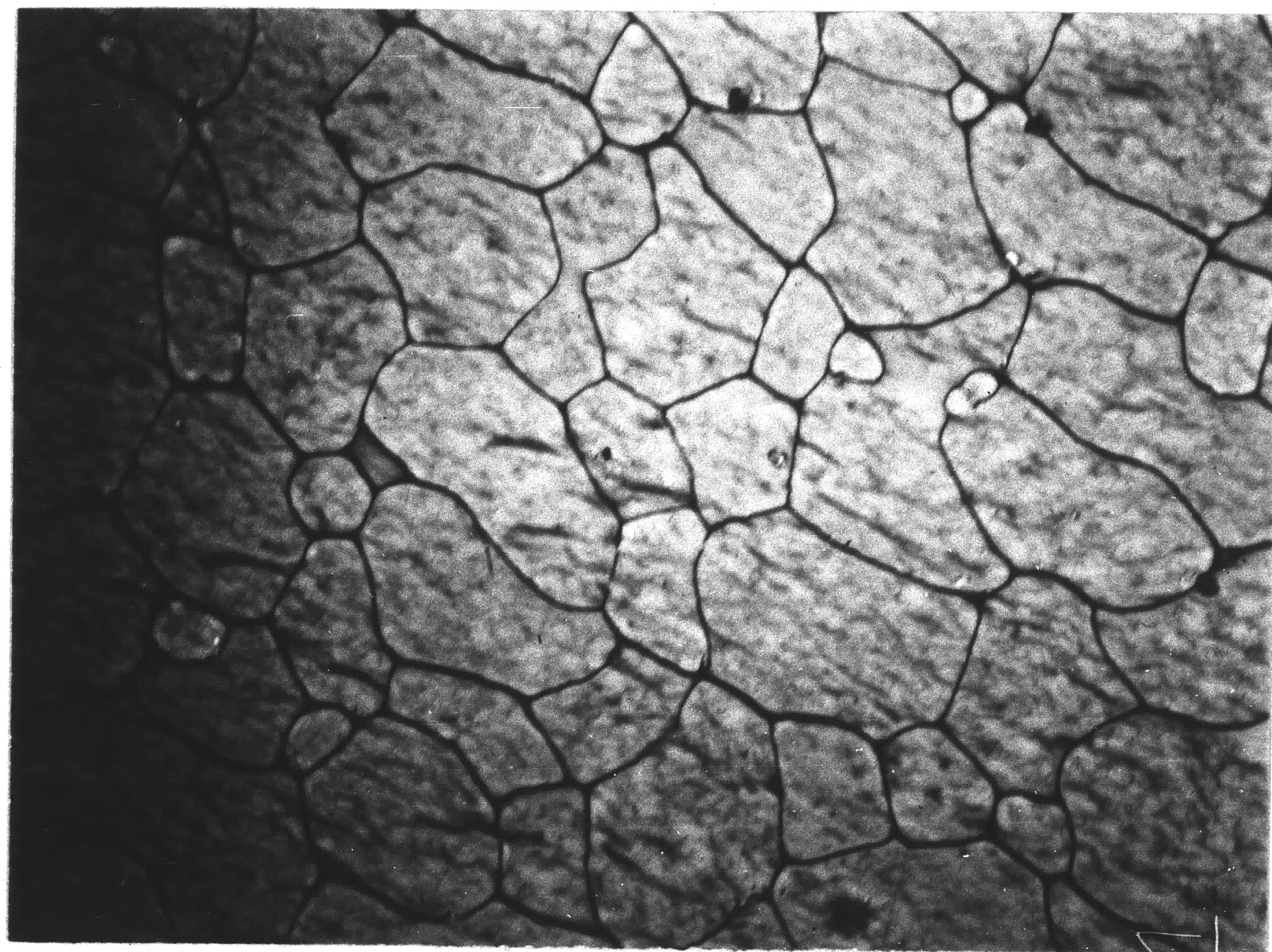
FIGURE 15

ELECTRON MICROGRAPH SHOWING THE MICROSTRUCTURE OF
HEAT TREATED PLZT, 1200°C - 6,000 MINUTES (3,800X)

observed to take place during heat treatment. Scanning electron micrographs of a typical heat treated specimen which has been polished and one which has been polished and thermally etched is given in Figures 16-18. The presence of artifacts and polishing scratches can be observed in the micrographs, but they indeed substantiate the microstructural features revealed by the replica technique. In general, all the micrographs clearly illustrate that the heat treated specimens retain the basic microstructural characteristics of the initial pressure-sintered material, i.e., no exaggerated grain growth.
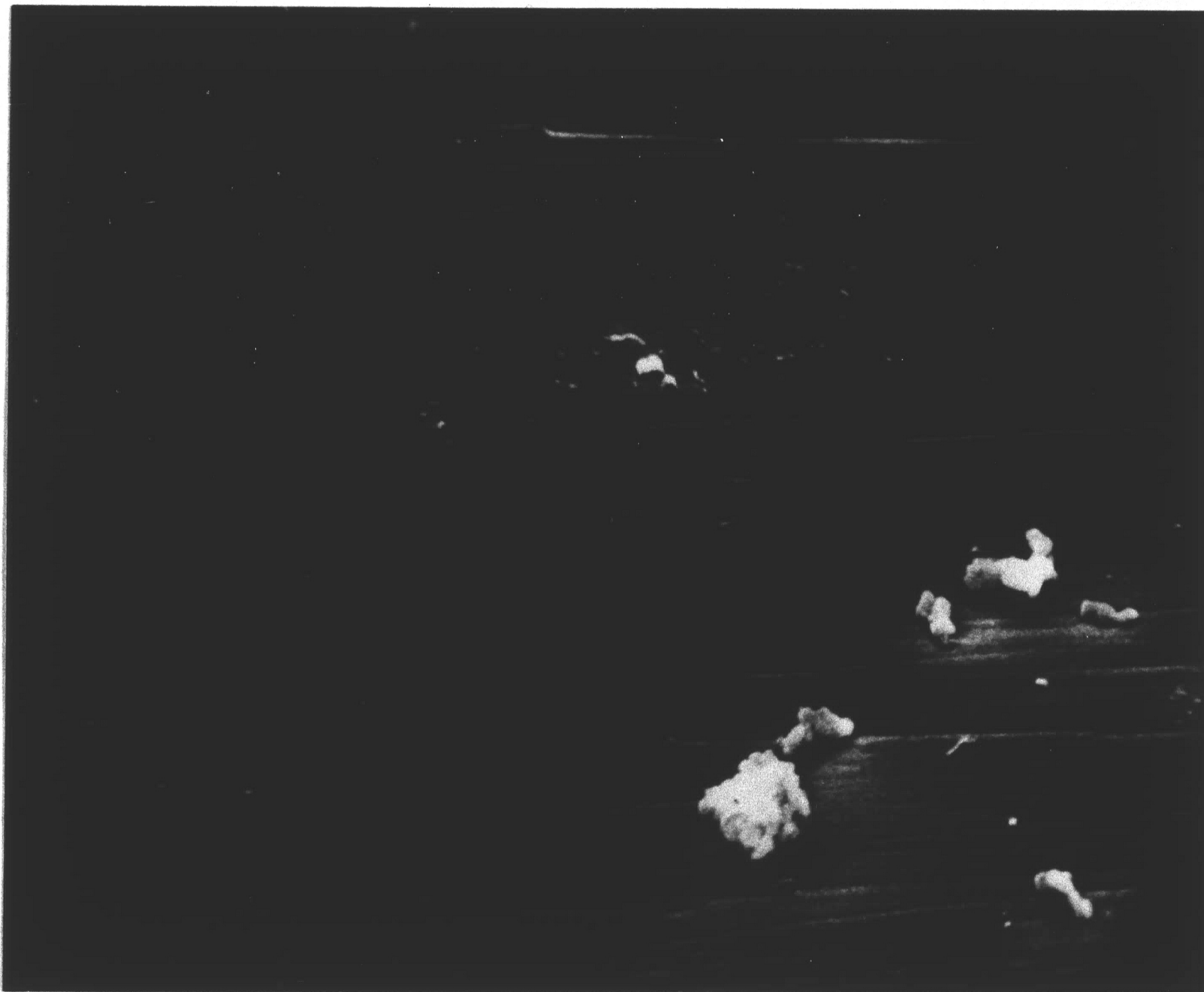
FIGURE 16

SCANNING ELECTRON MICROGRAPH OF A TYPICAL HEAT TREATED (1200°C-
4,320 MINUTES) SPECIMEN WHICH HAS BEEN POLISHED (5,250X)

FIGURE 17
SCANNING ELECTRON MICROGRAPH SHOWING A TYPICAL HEAT TREATED SPECIMEN
(1250°C-1,920 MINUTES) WHICH HAS BEEN THERMALLY ETCHED (2,100X)
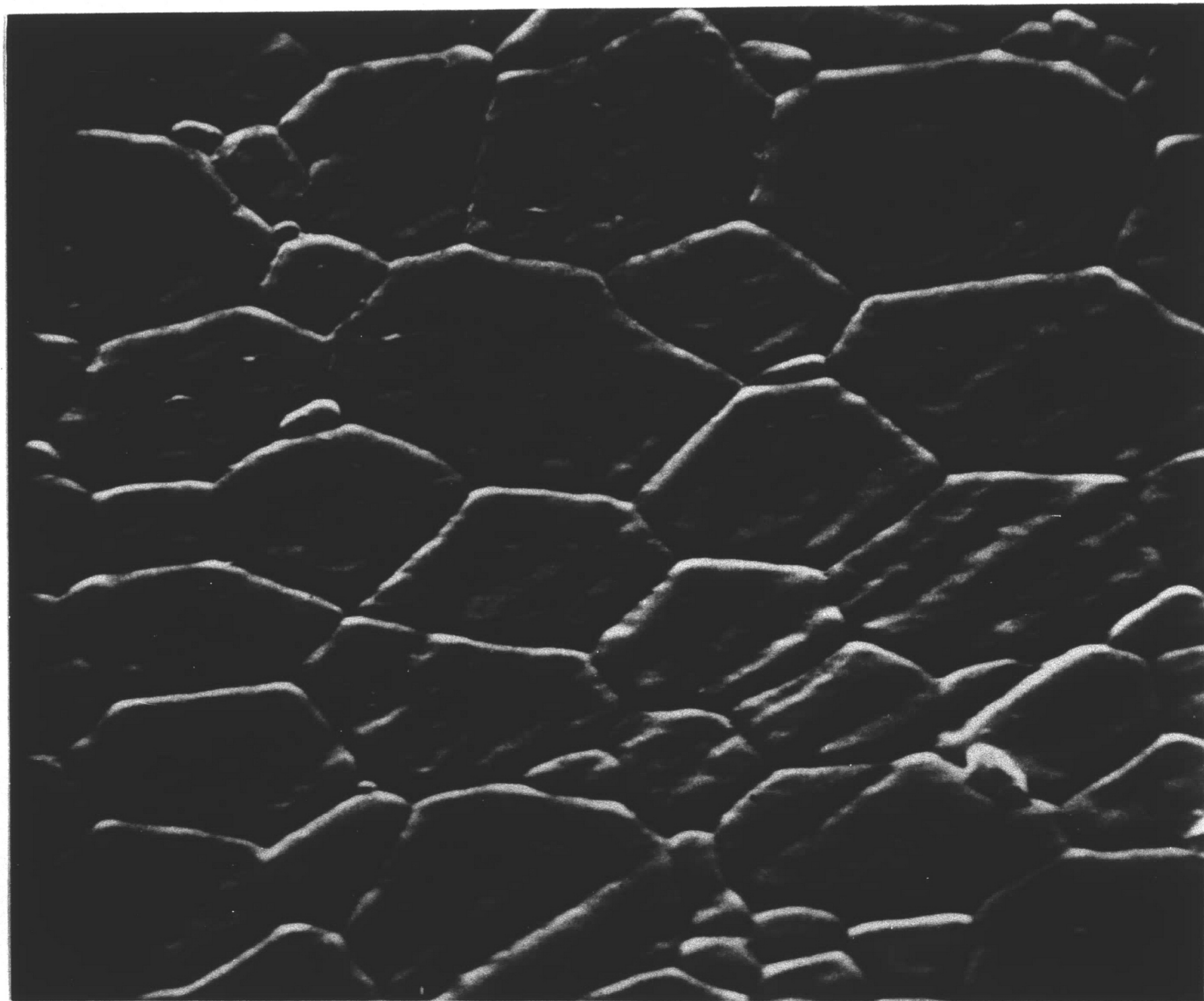
FIGURE 18
SCANNING ELECTRON MICROGRAPH SHOWING A TYPICAL HEAT TREATED SPECIMEN
(1250°C-1,920 MINUTES) WHICH HAS BEEN THERMALLY ETCHED (5,250X)

4. Electrical and Electromechanical Properties

The effect of microstructure on the physical properties was investigated by isothermally heat treating fully dense specimens as discussed previously in sections II-4 and III-2. The specimens utilized in this investigation were heat treated at 1100°C, 1200°C, and 1250°C, and experienced weight losses (see Table III) as a consequence of the equilibration process. In all instances the weight losses were less than 2.6 weight percent and thus these specimens were considered to be in the single-phase field as discussed previously in section III-2.

The initial pressure-sintered slugs utilized in this investigation had average grain diameters of 1.1 ± 0.1 μm. Property measurements were performed on the disks originating from both the end and the center of each slug. Evaluation of the poled properties within a given slug revealed that in every case the center disk displayed slightly higher values for k_p and K_3^T, and slightly lower values for the dissipation factor (D.F.) relative to the end disk. Typical property differentials between the center and end disks within a slug were 0.03 for k_p, 100 for K_3^T, and 0.0020 for the D.F. The maximum deviation observed in one slug was 0.06, 277, and 0.0040 for k_p, K_3^T, and D.F. respectfully. Table V gives the initial properties of all the pressure-sintered slugs utilized.

In order to insure that the observed properties of the pressure-sintered disks were not in some fashion altered by the influence of

TABLE V

INITIAL ELECTRICAL AND ELECTROMECHANICAL PROPERTIES
OF THE PRESSURE-SINTERED SLUGS

Property		Pressure-Sintered Specimens
k_p		0.535 ± 0.045
K_3^T	Unpoled	2234 ± 146
	Poled	2120 ± 140
D.F.($\tan \delta$)	Unpoled	0.0230 ± 0.0027
	Poled	0.0240 ± 0.0040

residual stresses due to the fabrication process, machining, etc.
the samples were annealed. The annealing procedure consisted of
taking the disks above their Curie temperature ($\approx 150^{\circ}C$) and slowly
cooling them. Upon re-evaluation of the properties 24 hours after
poling it was generally observed that the annealing produced only
slight property variations which were within the experimental error
of the measurements.

It was found experimentally that when disks were selected ran-
domly and heat treated, the resultant properties of these disks were
not dependent upon the position of the disk within the original
slug. For example, the slug which exhibited the greatest differ-
ence between the properties ($\Delta k_p = 0.06$ and $\Delta K_3^T = 277$) of center
and end samples became very uniform ($\Delta k_p = 0.01$ and $\Delta K_3^T = 73$) upon
heat treating at $1200^{\circ}C$ for 480, 1920, and 6120 minutes.

The dielectric constant prior to poling is plotted in Fig.
19A as a function of the average grain diameter. In all instances
it was observed that the dielectric constant of the unpoled pres-
sure-sintered material was of a lower value than that of the heat
treated specimens. No consistent variation of the unpoled di-
electric constant with grain diameter was observed in this study.
However, it has been commonly observed in PZT systems (19,29), with
similar grain diameter ranges, that the dielectric constant de-
creases with increasing grain diameter. This effect in $BaTiO_3$
has been explained by Buessum and co-workers (49) on the basis of

FIGURE 19

DIELECTRIC CONSTANT (K_3^T) UNPOLED (A) AND POLED (B)
AS A FUNCTION OF AVERAGE GRAIN DIAMETER
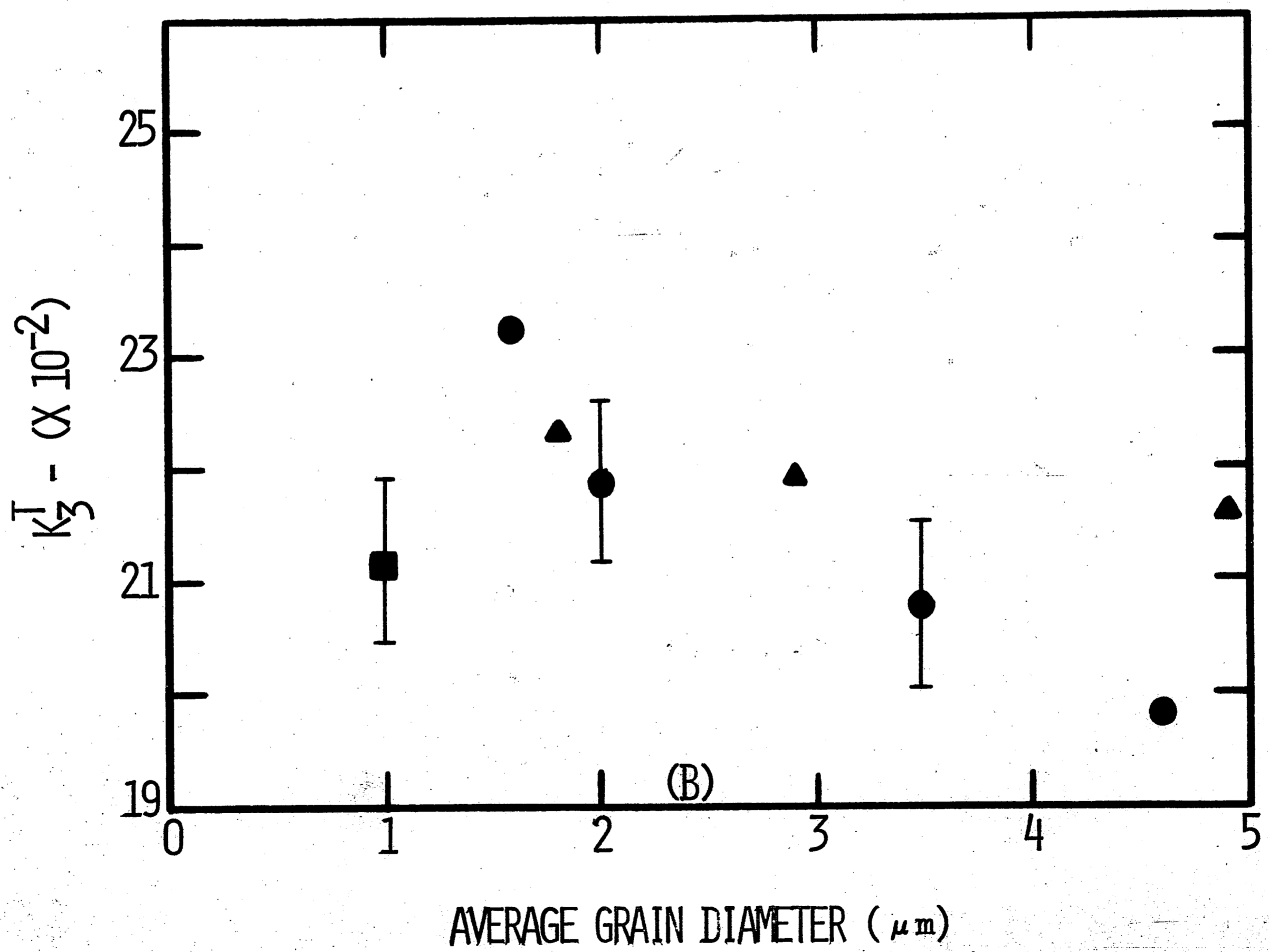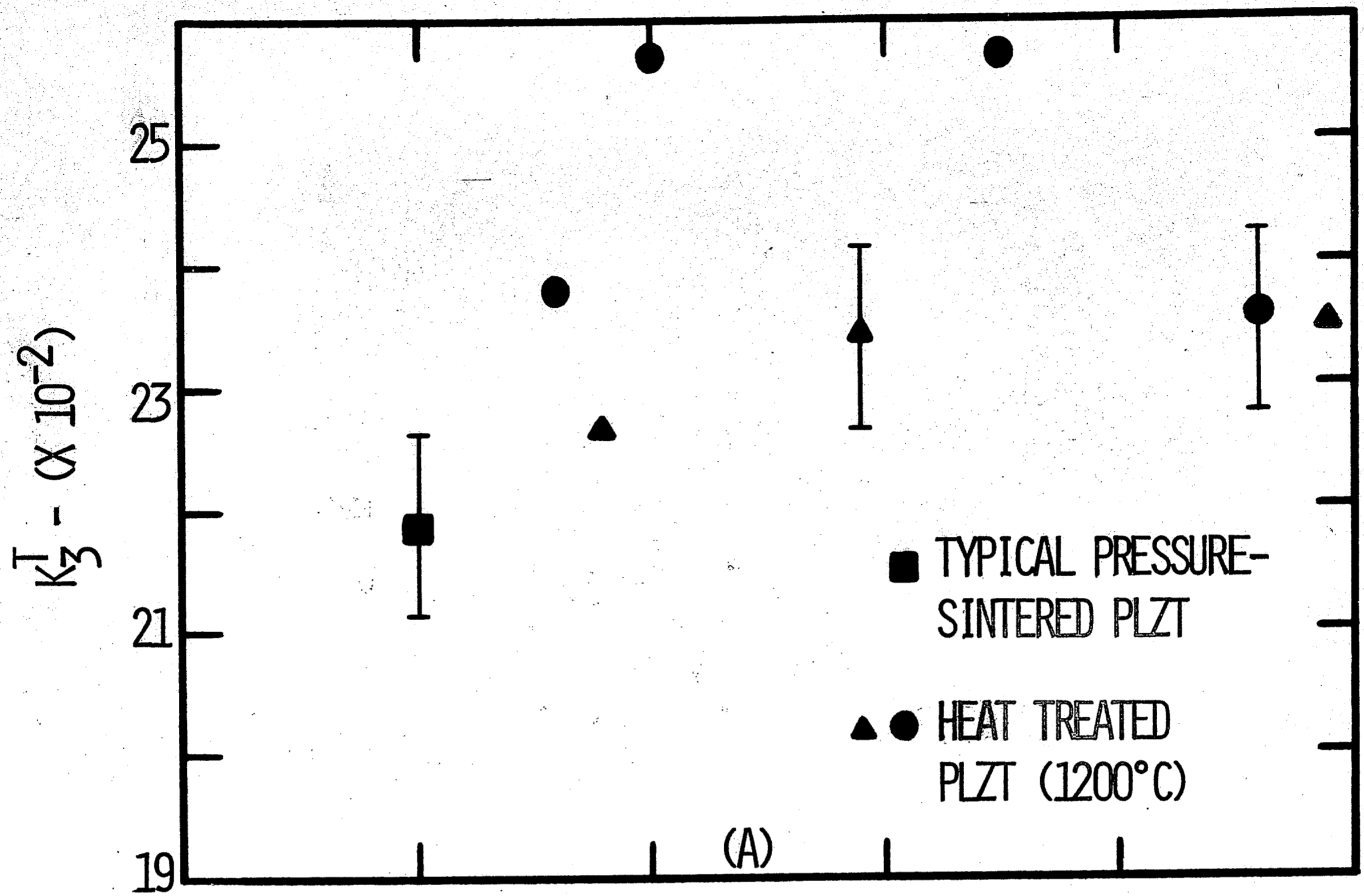
internal stresses developed on passing through the Curie tempera-
ture. A larger grain diameter is thought to facilitate the reduc-
tion of stresses by the development of 90° domains within the
grain, while a grain diameter approaching the size of the domains
make this impossible.

On the basis of the experimental data in this work one would
expect the domain size of the material to be relatively small
compared to the grain size. Thus, an attempt was made to reveal the
domain texture of the material and this is given in Fig. 20. Al-
though the scanning electron micrograph does indeed confirm the
presence of a fine domain texture further experimental studies
should be conducted in order to conclusively establish the precise
domain texture in PLZT materials.

The poled dielectric constant is plotted as a function of the
average grain diameter in Fig. 19B. A slight trend towards lower
dielectric constants with increasing grain diameter, for the heat
treated specimens, is suggested. However, this effect is near the
experimental error. Therefore, it was not considered useful to
attribute this trend to a definite mechanism. Similar trends have
been observed in PZT materials previously and explainations have
been proposed (29).

The unpoled dissipation factor is plotted in Fig. 21A as a
function of the average grain diameter. In all instances the heat
treated specimens displayed higher values for the dissipation
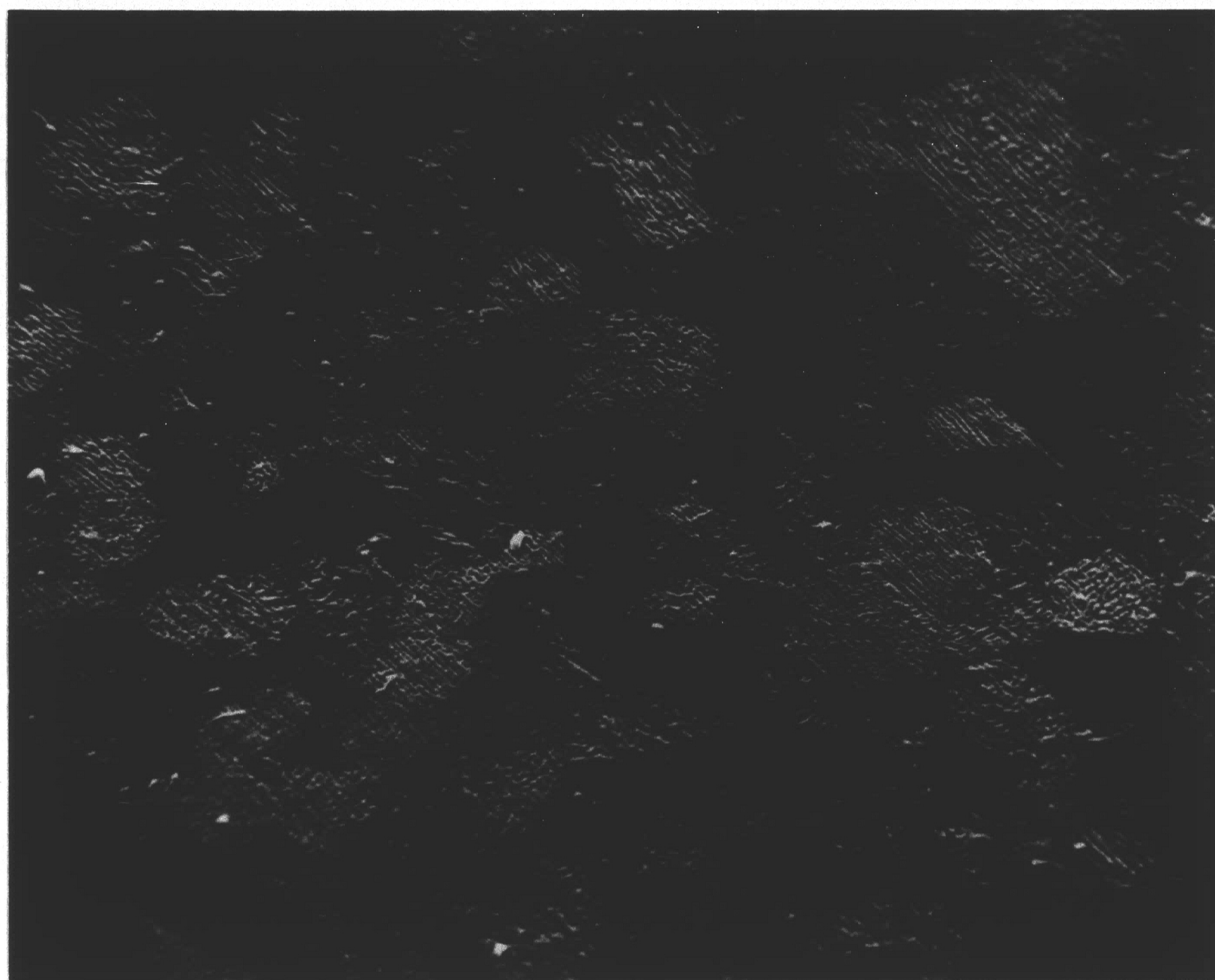
FIGURE 20

SCANNING ELECTRON MICROGRAPH SHOWING THE DOMAIN TEXTURE IN A
TYPICAL HEAT TREATED (1200°C-4,320 MINUTES) SPECIMEN (2,100X)

FIGURE 21
DISSIPATION FACTOR UNPOLED (A) AND POLED (B)
AS A FUNCTION OF AVERAGE GRAIN DIAMETER
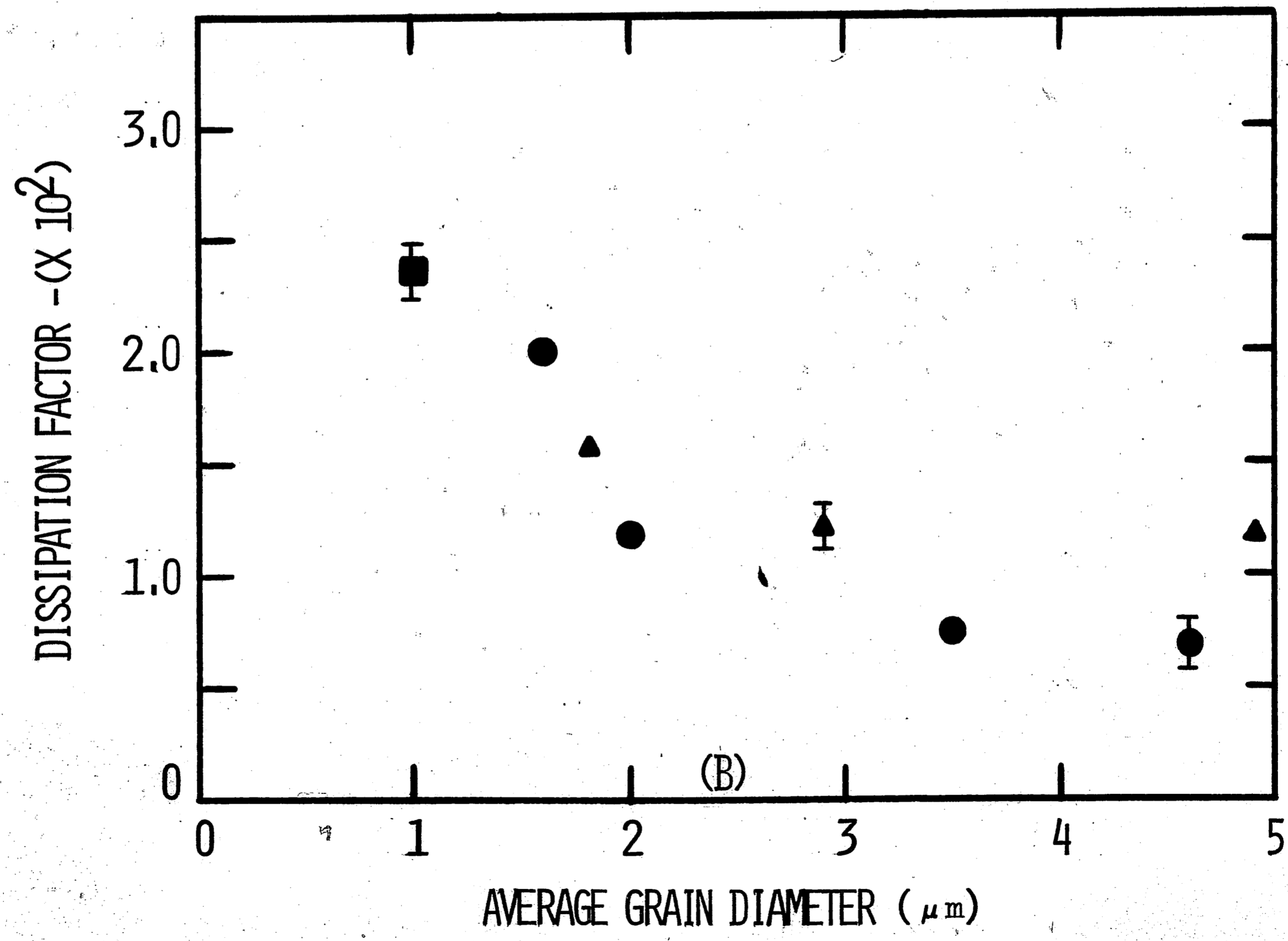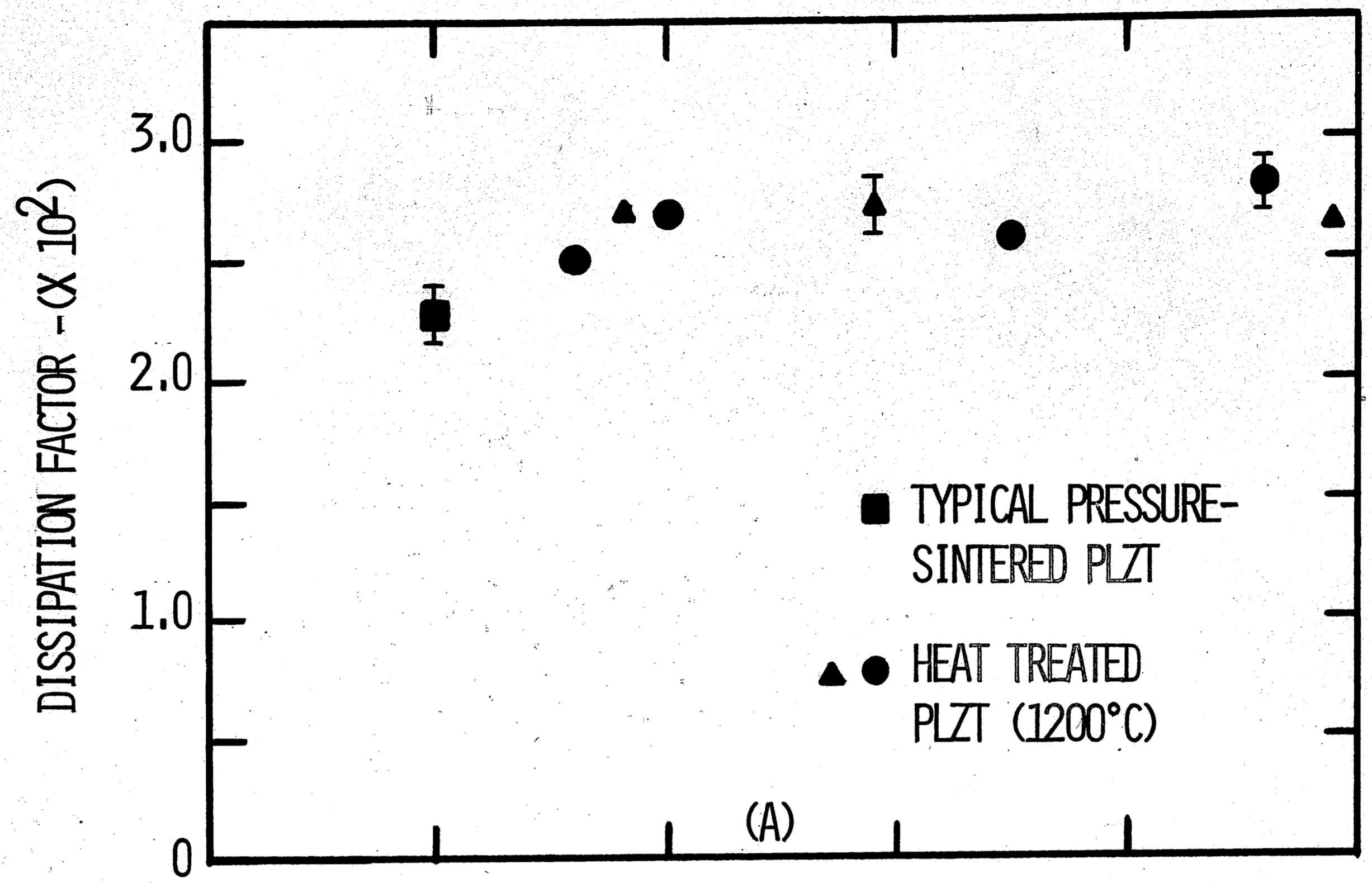
factor than that of the pressure-sintered specimens. No grain

diameter effects upon the unpoled dissipation factor were in

evidence.

The poled dissipation factor is plotted in Fig. 21B and prop-

erty variation is observed to be dependent upon the average grain

diameter. Similar grain diameter effects have been observed in

PZT systems (6, 19, 29), but no conclusive explanations have thus

far been proposed.

The planar coupling factor (k_p) is plotted as a function of

average grain diameter in Fig. 22. The coupling factor (which is

proportional to the remanent polarization) increases with heat

treatment, but is observed to become relatively constant with in-

creasing grain diameter. In previous studies (20, 29) it has been

observed that domain re-orientation in fine-grained material is

inhibited and thus leads to a lower remanent polarization. This

effect is not observed to be present in the heat treated specimens

with grain sizes ranging from 1.5 μm to 4.9 μm. However, a

significant increase in the planar coupling factor of the pressure-

sintered material is achieved in going from $\approx$ 1 μm to 1.5 μm.

This may be attributable to grain diameter effects, although this

is not very probable (see Fig. 20). The most probable mechanism

producing this increase in the planar coupling factor is the si-

multaneous stoichiometry change taking place during heat treatment.

This will be discussed later.
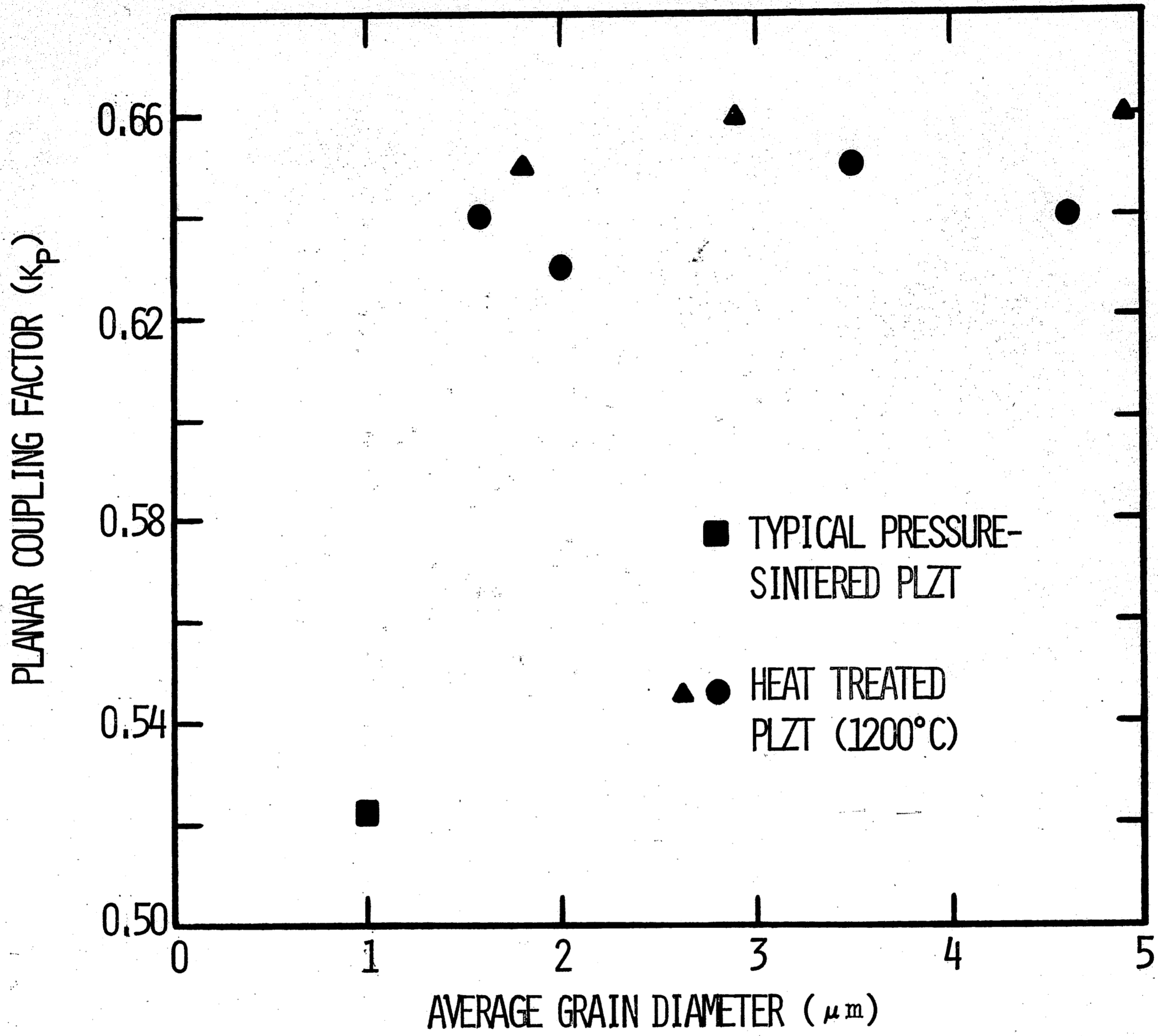
FIGURE 22

PLANAR COUPLING FACTOR (κ_p) AS A FUNCTION OF
AVERAGE GRAIN DIAMETER

The resonant frequency of the pressure-sintered material was observed to shift to lower frequency values upon heat treatment. This shift corresponds to a lowering of the mechanical stiffness of the pressure-sintered material. However, the resonant frequency was observed to be relatively constant in all the heat treated specimens and hence independent of the heat treatment temperature and grain diameter. The independence of the resonant frequency with grain diameter in fully dense materials has been previously established (50). It is therefore felt that the initial shift in the resonant frequency is not due to the increase in the grain diameter, but rather to an initial stoichiometry change (approximately $\leq$ 1 weight percent loss) experienced by the heat treated specimens.

The relative dielectric constant is plotted as a function of temperature in Figures 23 and 24 for specimens of various average grain diameters. The initial pressure-sintered material used in this study was observed to be comparable to the values reported in the literature by Haertling and Land (23). The relative dielectric constant reported for a 7/65/35 composition was approximately 12,000 at 150°C, this value is observed to be in excellent agreement with the data obtained in the present study. The effect of increasing grain diameter was to increase the relative dielectric constant at the Curie temperature. It is believed that this effect is due to the greater domain wall motion at low fields (1kHz) within the

FIGURE 23

DIELECTRIC CONSTANT AS A FUNCTION OF TEMPERATURE
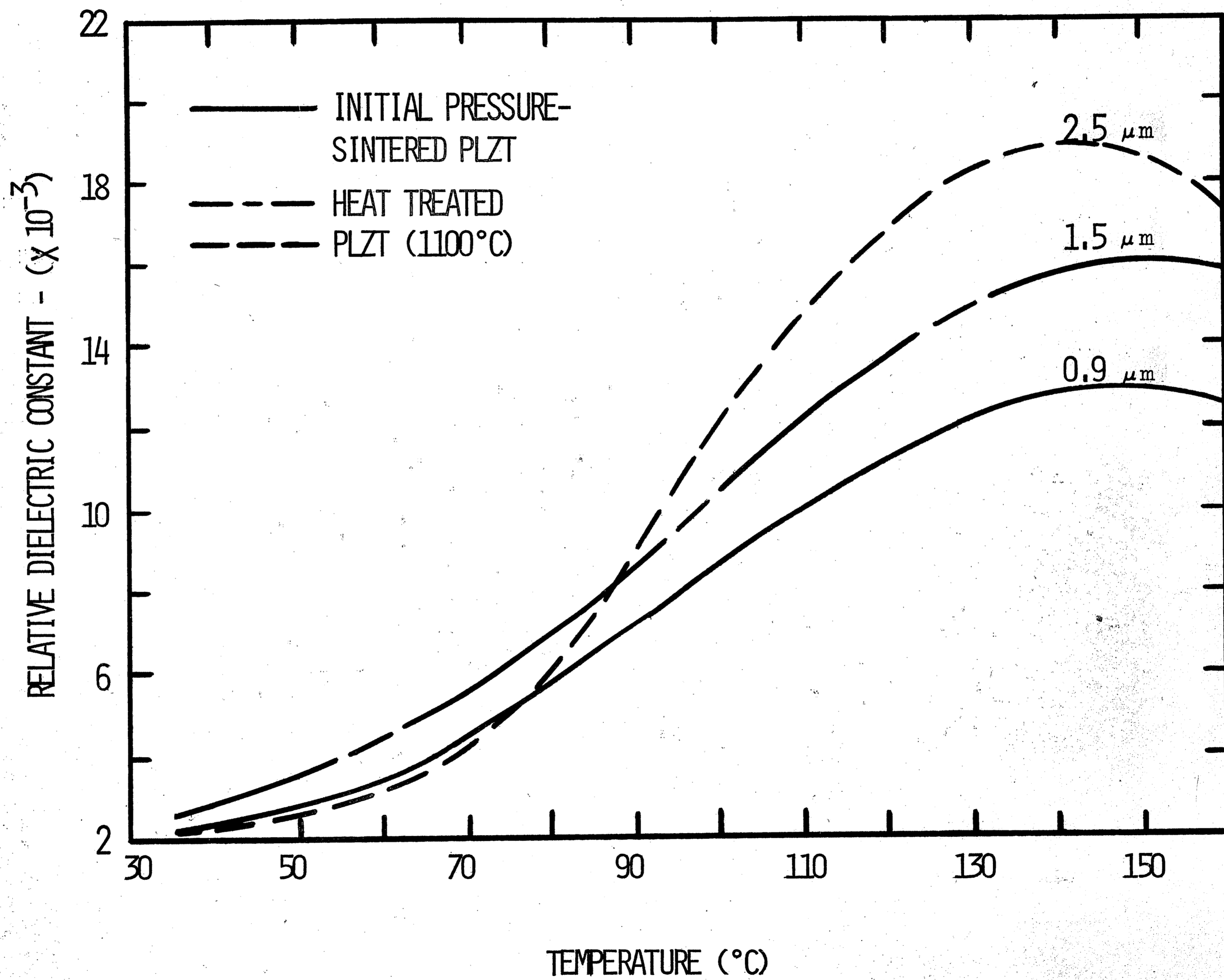
FIGURE 24

DIELECTRIC CONSTANT AS A FUNCTION OF TEMPERATURE

55
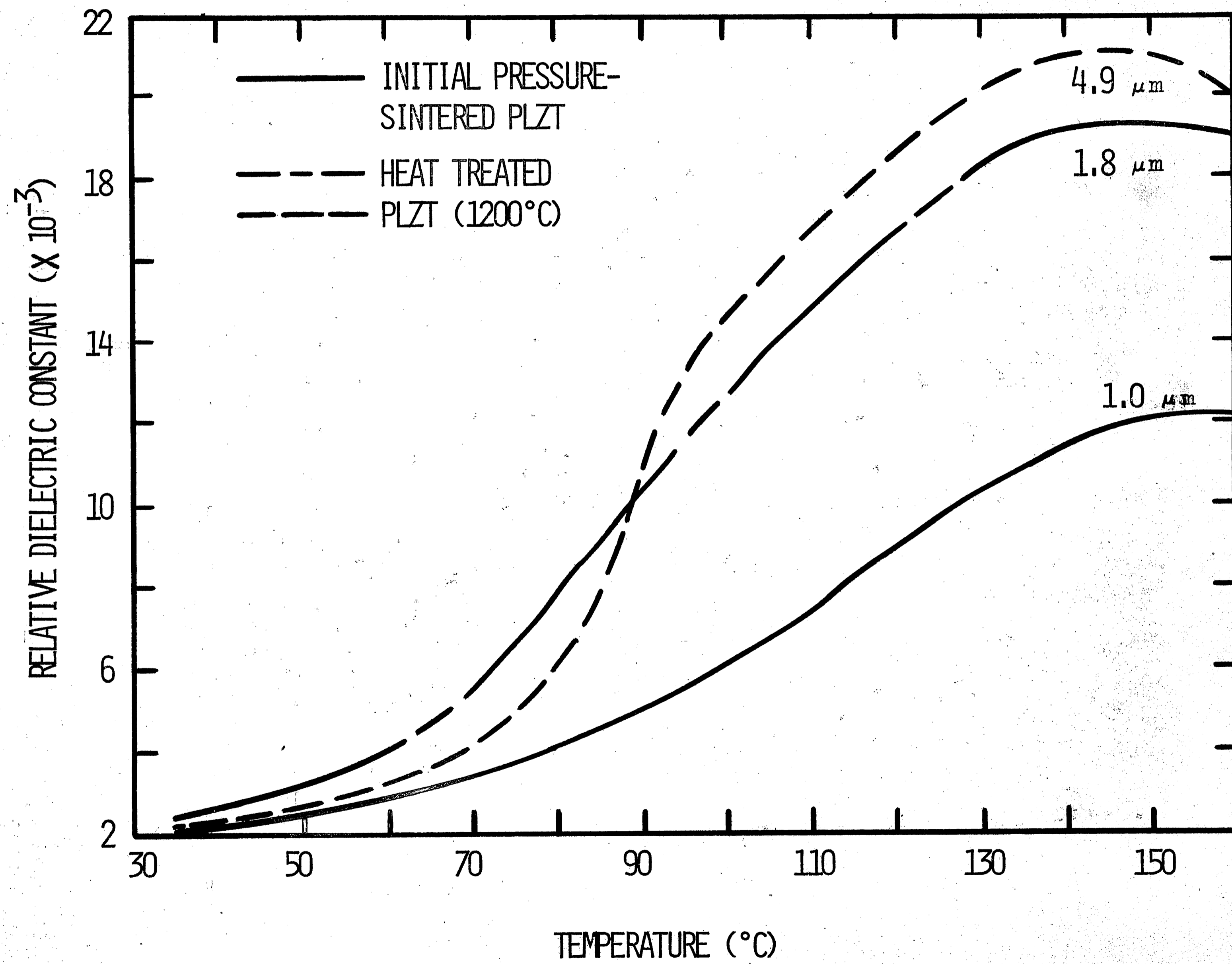
large grain material.

Slight shifts in the relative dielectric constant peak towards lower ($\approx 10^{\circ}$C) temperatures was observed in certain heat treated specimens given in Figures 23 and 24. The experimental procedure of monitoring the capacitance as a function of temperature used for this work was not well suited for the precise determination of the Curie temperature for PLZT materials. Therefore, further investigation of this trend towards lower Curie temperatures is necessary. The present data should be interpreted with care.

The values determined for the relative dielectric constant at the Curie temperature are plotted as a function of the average grain diameter in Fig. 25. The relative dielectric constant at the Curie temperature is dependent upon the specimens grain size and independent of the heat treatment temperature utilized to obtain this grain size. The curve drawn through the data points is only a visual estimate.

The dissipation factor was also measured as a function of temperature during the previously mentioned measurements. This data is plotted in Figures 26 and 27.

With respect to the observed property variation induced by the isothermal heat treatment, one must carefully consider all the possible mechanisms which may contribute to this variation. The three mechanisms thought to be of significant consequence to this study are: (1) the effect of grain size on the materials domain

FIGURE 25

RELATIVE DIELECTRIC CONSTANT AT THE CURIE TEMPERATURE AS A
FUNCTION OF AVERAGE GRAIN DIAMETER
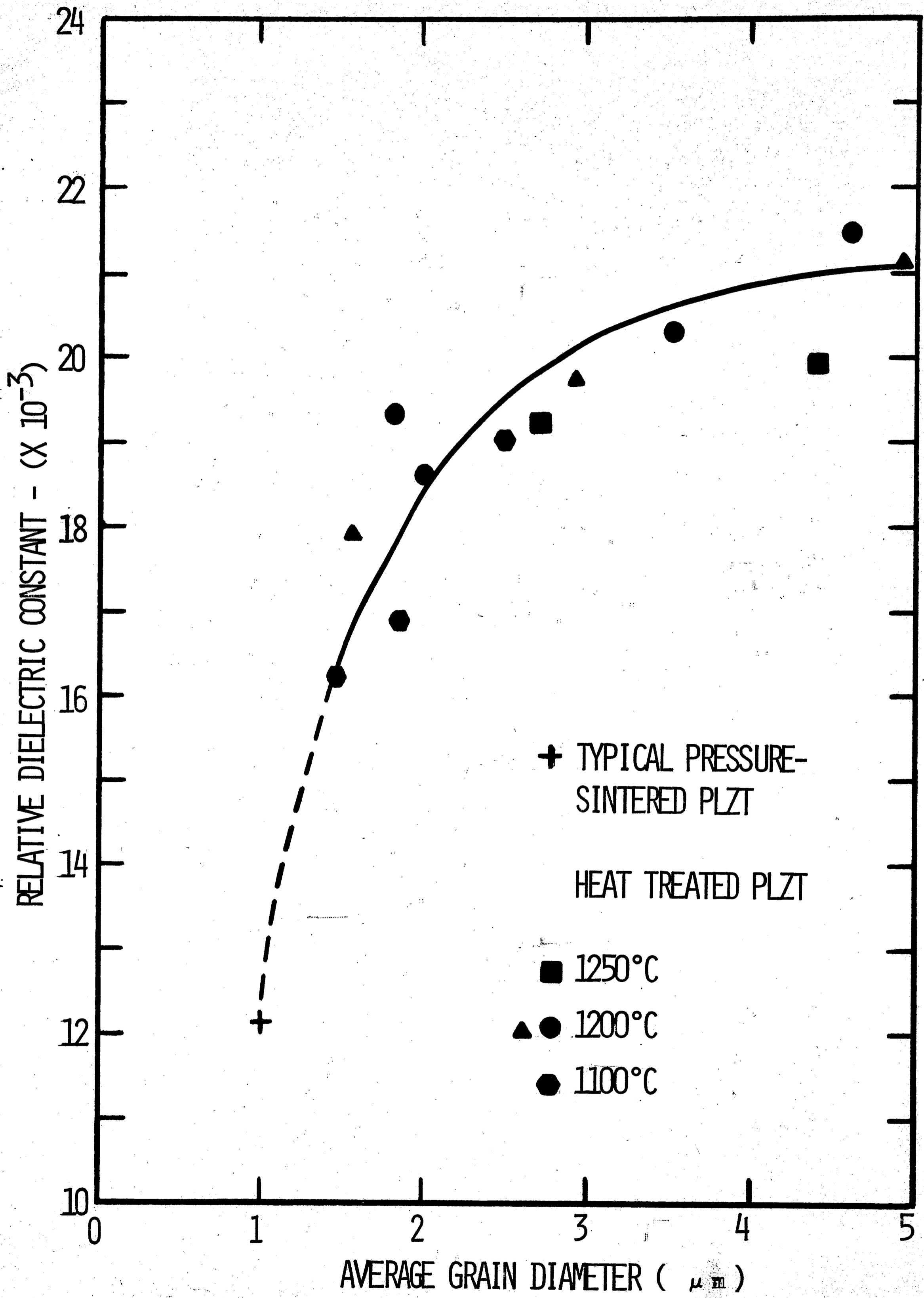
FIGURE 26

DISSIPATION FACTOR AS A FUNCTION OF TEMPERATURE
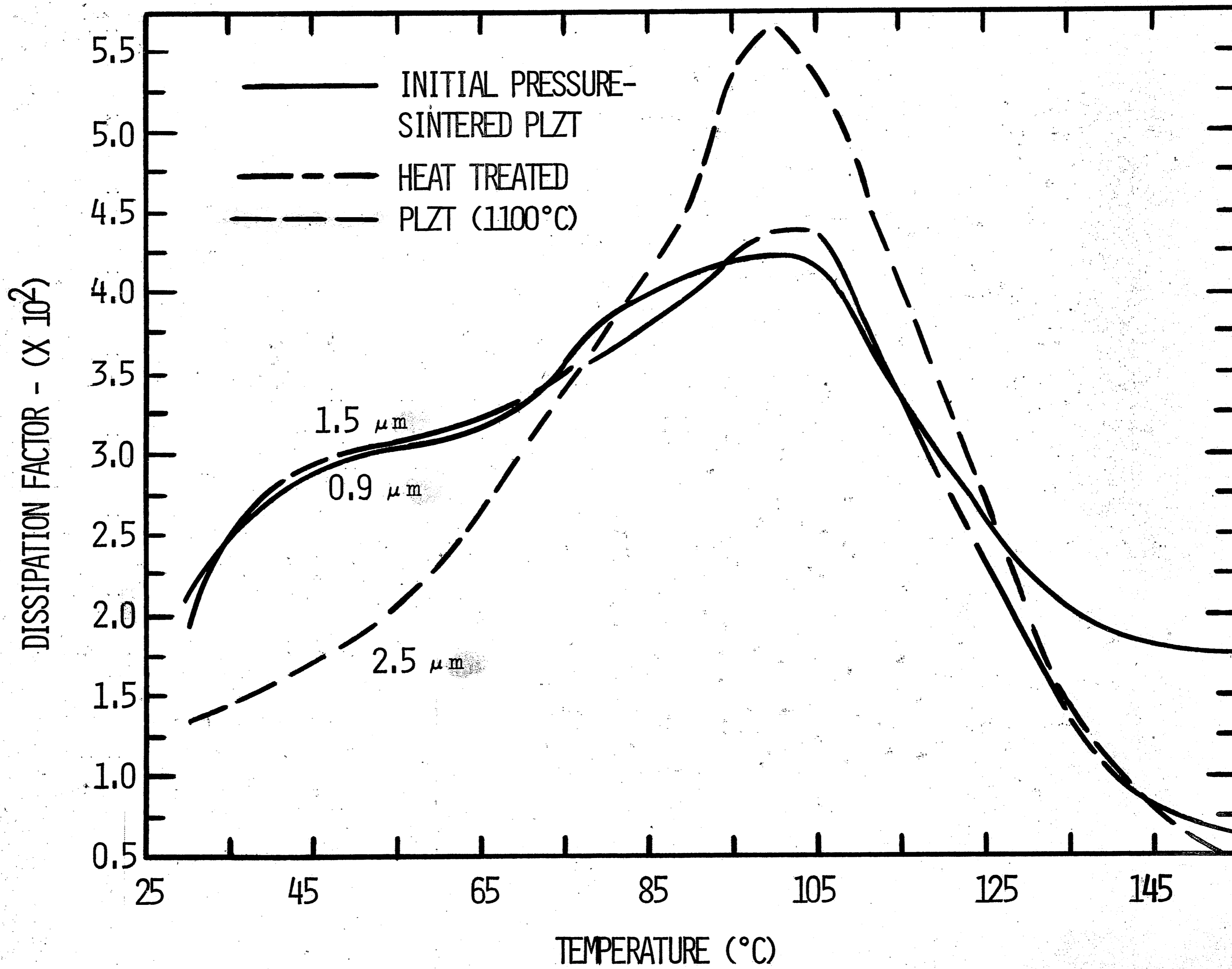
FIGURE 27

DISSIPATION FACTOR AS A FUNCTION OF TEMPERATURE
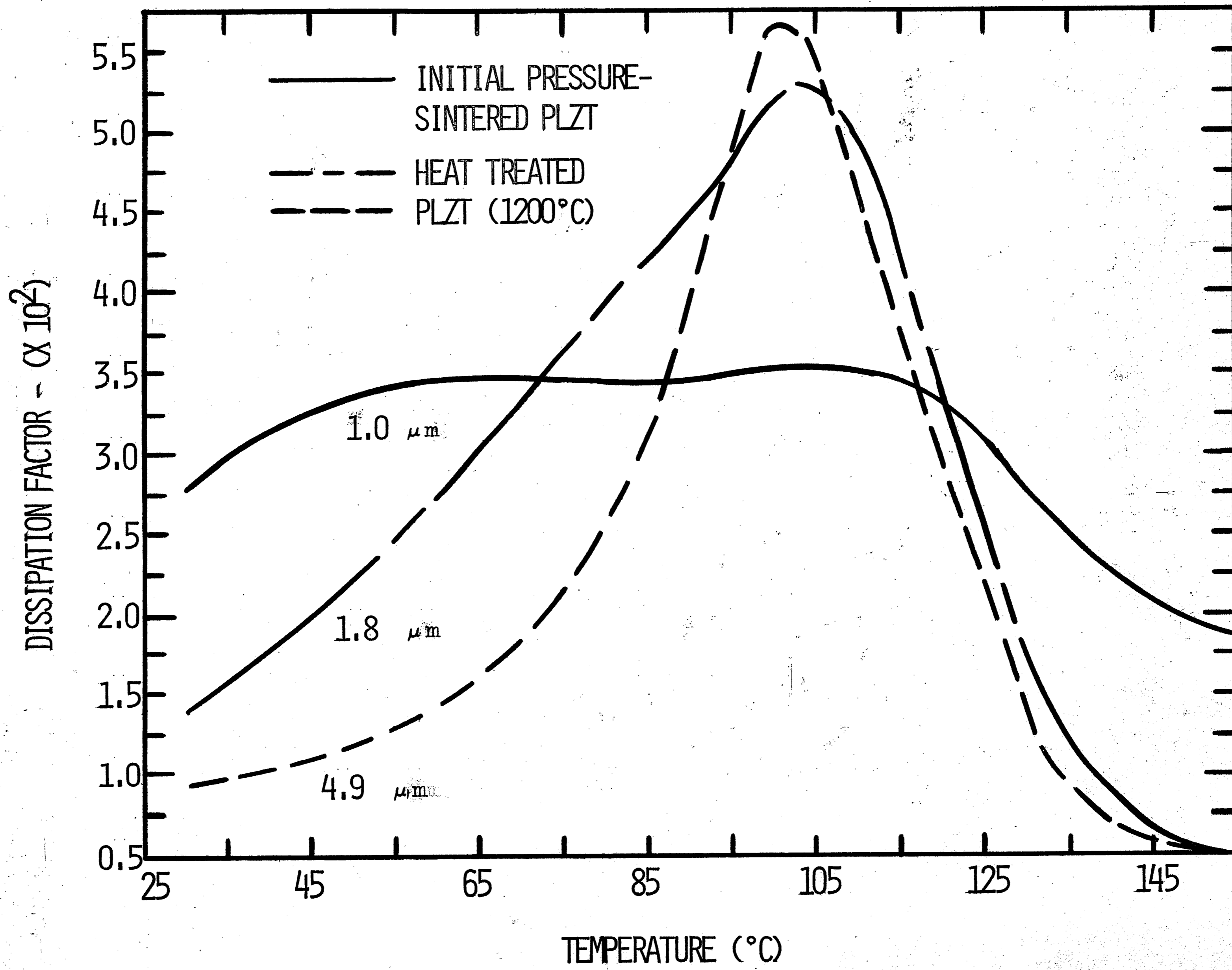
texture, (2) the effect of stoichiometry changes (due to PbO losses during heat treatments) within the single-phase field on the domain wall motion, and (3) the loss of a sufficient amount of PbO to cause a compositional shift at high temperatures towards the rhombohedral-tetragonal phase boundary and the corresponding precipitation of a second phase. Of course any of the above may be occurring simultaneously.

The effect of grain diameter on a ferroelectric materials domain texture and domain wall mobility has been discussed previously in the text. Generally, these effects are related to the relative ease with which internal stresses can be relieved by a change in domain configuration. Therefore, property variation may be expected to occur if the domain size approaches the grain diameter making re-orientation of the domains difficult. This mechanism is probably not important here since the grain diameter appears to be much larger than the domain size.

The effect of stoichiometry variation due to the presence of Pb and O lattice vacancies on the ferroelectric behavior of doped and undoped PZT ceramics has been investigated (9, 51). In a similar PZT doped (Bi^{+3}) system the remanent polarization was observed to increase upon rapid cooling from the sintering temperature and upon annealing in low Pb or O activity atmospheres. The observed increase in the remanent polarization of the bismuth doped PZT was attributed to an increase in the concentration of point

defects. Therefore, considering the experimental heat treating conditions employed in the present study, i.e. annealing in a low PbO activity atmosphere followed by a rapid quench, it is highly probable that the observed increase in k_p is facilitated by the introduction of point defects within the pressure-sintered material.

Property variations as a function of compositional change in the PLZT system has been investigated by Haertling and co-workers (23, 24). The PLZT phase diagram indicates that there are three possible paths by which a composition in the rhombohedral ferro-electric region can be modified such that it approaches the rhombohedral-tetragonal phase boundary. These three paths and the associated trends in property variation for a 7/65/35 PLZT composition are summarized in Table VI.

The experimental evidence of this work does not substantiate the mechanism by which property variation is achieved by means of a compositional shift towards the rhombohedral-tetragonal phase boundary. Since PbO loss during the equilibration process is the means by which a compositional shift would be accomplished, one would expect the properties to be dependent upon the amount of PbO lost by the specimen. Therefore, with increasing PbO loss, which corresponds to increasing isothermal heat treatment tempera-ture, one would expect to observe increasing values for K_3^T and k_p. However, in the range measured this dependence of the properties was not observed. In general the determined values for K_3^T (poled

TABLE VI

Possible Paths By Which A Nominal 7/65/35 PLZT Composition
Can Approach The Rhombohedral-Tetragonal Phase Boundary And
The Effect of These Paths On Properties

Property	Path 1* 7 + X/65/35	Path 2* 7/65 - Y/35 + Y	Path 3* 7 + X/65 - Y/35 + Y
K_3^T	Sharp Increase	Increase	Increase
k_p	Increase	Increase	Increase

*Where X and Y are positive values

and unpoled), D.F. (poled and unpoled), and k_p were relatively
constant (discounting grain size effects on the poled value of the
D.F.) regardless of the heat treatment temperature providing further
evidence of stoichiometry accomodation within the single-phase
field.

On the basis of the experimental data obtained in this study
and the findings previously cited in the literature it is thought
that two mechanisms are responsible for the observed property
variation. These two mechanisms are grain diameter effects and
lattice vacancy effects. Grain diameter effects have been shown
to be important as they relate to the poled dissipation factor and
the dielectric constant at the Curie temperature.

The initial increase in the unpoled and poled dielectric
constant, unpoled dissipation factor, and the planar coupling
factor observed upon heat treating a pressure-sintered specimen, is
thought to be dependent upon the initial stoichiometry change
(approximately 1 weight percent loss). As expected the degree of
stoichiometry change was observed to have little influence on the
properties, since the difference in activities at the various
temperatures is small (9) compared to the difference from the
as-sintered samples. Therefore, there will be little property
variation, as observed in the present study, between the specimens
heat treated at various temperatures.

IV. CONCLUSIONS

(1) Pressure-sintering conditions have been determined to produce theoretically dense PLZT specimens with average grain diameters of $\approx 1\,\mu m$.

(2) Isothermal grain growth of fully dense, single-phase PLZT (7/65/35) in the presence of a low activity atmosphere (PbO) obeys the $D^3 - D_o^3 = k't$, relationship. The mechanism controlling the grain growth rate is thought to be due to a solid solution (impurity) drag. The phenomenological activation energy for grain growth was calculated to be 86 K cal./mole.

(3) Grain diameter effects were observed to be important only as they relate to the poled dissipation factor and the relative dielectric constant at the Curie temperature. In the range studied ($1\,\mu m - 4.9\,\mu m$) the dissipation factor was shown to decrease with increasing grain diameter, while the dielectric constant at the Curie temperature increased with increasing grain diameter.

(4) The isothermal heat treatment of pressure-sintered PLZT specimens, as performed in this study, increased the planar coupling factor approximately 20% in value, while the small signal dielectric measurements remained relatively constant (discounting grain diameter effects as mentioned above). This increase in the planar coupling factor is believed to be due to the introduction of point defects into the PLZT lattice.

(5) Single-phase PLZT exists over a range of stoichiometries
corresponding to varying concentrations of lattice vacancies.
Electrical and electromechanical properties were relatively in-
sensitive to the degree of the stoichiometry change (as monitored
by the sample weight loss) in the range measured (0.95% - 2.55%).

APPENDIX I

ELECTRICAL AND ELECTROMECHANICAL DATA

Heat Treating Temperature°C	Time (Minutes)	Grain Dia.(μm)	%weight Change	Disk Number*	Prior to Poling		24 hours after poling		
					K_3^T	D.F.	K_3^T	D.F.	k_p
–	0	0.9	0	1	2220	0.0207	2128	0.0245	0.55
–	0	0.9	0	5	2380	0.0226	2233	0.0225	0.58
1100	480	1.5	1.08	3	2521	0.0268	2420	0.0207	0.62
1100	1920	1.9	1.37	6	2510	0.0268	2387	0.0181	0.65
1100	6000	2.5	0.95	2	2389	0.0266	2090	0.0150	0.64
–	0	1.0	0	7	2119	0.0206	2075	0.0232	0.49
–	0	1.0	0	4	2180	0.0203	2150	0.0200	0.52
1200	180	1.6	1.62	2	2380	0.0250	2327	0.0200	0.64
1200	480	2.0	1.79	5	2569	0.0270	2186	0.0117	0.63
1200	1950	3.5	1.75	6	2570	0.0258	2076	0.0075	0.65
1200	6030	4.6	1.95	3	2361	0.0283	1983	0.0070	0.64
–	0	1.0	0	1	2088	0.0256	1980	0.0279	0.51
–	0	1.0	0	4	2347	0.0243	2257	0.0239	0.57
1200	480	1.8	1.71	2	2267	0.0271	2234	0.0157	0.65
1200	1920	2.9	1.94	3	2344	0.0274	2189	0.0123	0.66
1200	6120	4.9	1.80	5	2353	0.0265	2161	0.0120	0.66
–	0	1.1	0	1	2198	0.0251	2126	0.0260	0.52
–	0	1.1	0	4	2357	0.0243	2245	0.0255	0.55
1250	480	2.7	2.55	2	2409	0.0302	2223	0.0149	0.65
1250	1920	4.4	2.41	5	2511	0.0293	2144	0.0114	0.64

*Disks numbered 3 and 4 originate from the approximate center of the pressure-sintered slug, while disks numbered 1 and 7 originate from the ends.

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