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# QUANTIZING THE POLARIZATION OF LEAD ZIRCONATE-TITANATE

Scott W. Hewett
(M. S. thesis)

December 1977

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

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# QUANTIZING THE POLARIZATION OF LEAD ZIRCONATE-TITANATE

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# QUANTIZING THE POLARIZATION OF LEAD ZIRCONATE-TITANATE

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## ABSTRACT

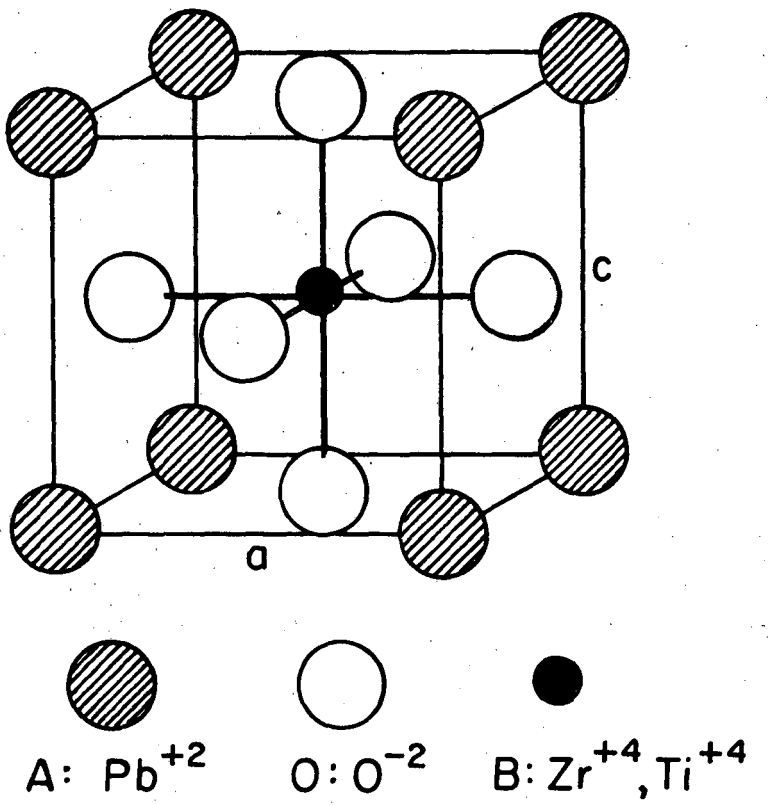
The polarization of polycrystalline lead zirconate-titanate ceramics was investigated. Thin disks were sintered from compacts of calcined lead zirconate-titanate with various stoichiometry and dopants. A packing powder technique was used to control lead oxide loss during firing. The charge displaced during poling was measured using a Sawyer-Tower circuit at various poling temperatures. The resonant and antiresonant frequencies were measured 24 hrs. after poling to determine the planar coupling coefficient and mechanical quality factor for all samples. It is shown that the saturation polarization for all undoped samples is 161 $\mu C/cm^2$ regardless of the poling temperature. This value is 82% of the saturation polarization estimated for a single crystal. The piezoelectric constants show no correlation with poling temperature in the range studied as long as saturation polarization is achieved. The electric field required for saturation polarization was plotted against temperature so that the required field could be estimated at any given temperature.

# INTRODUCTION

The lead zirconate-titanate (PZT) ceramics show strong piezoelectric effects at certain compositions. Such effects arise basically because of the creation of ferroelectric domains when a ceramic compound of suitable structure is formed and cooled below its Curie temperature. In PZT these domains are consequences of the non-centrosymmetric structure of the perovskite lattice (Fig. 1.). The central B-site ion does not repose exactly in the center of the unit cell, but is displaced from the center. This gives rise to a net dipole moment. The B-site ion forms the positive end of the dipole and the oxygen ions are believed to deform to act as the negative end of the dipole.

In ferroelectric material, these dipoles align themselves into ferroelectric domains. The effect is similar to the formation of magnetic domains in ferromagnetic materials. Electrostatic energy decreases with an increase in the number of domains, but energy is stored in the domain walls, so the splitting or growth of the domains continue until the total energy is at a minimum. Ferroelectric domains arise from the crystal structure. In a tetragonal perovskite lattice, the dipoles are formed along the cube edges (001), while in a rhombohedral lattice they are formed along the cross-cell diagonals (111). An important ramification of this is that strain may be associated with domain switching.

To make a piezoelectric material of PZT, it must be poled. Poling consists of applying an external electric field to force the ferroelectric domains that are aligned opposite to the applied electric field to grow at the expense of those domains that are aligned with the field. The alignment opposite to the field minimizes the applied field energy by creating a dipole opposing it.

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The perovskite structure, $ABO_3$, as shown by $Pb(Zr, Ti)O_3$ above its Curie point. Below the Curie point $c/a \approx 1.02$.

Fig. 1

The change in alignment proceeds by movement of the central ion from one position to another. The desired effect of the poling process is to permanently align as many of these B-site ions as possible so that after the poling process is completed, the ceramic sample retains a net dipole frozen into the structure of the ceramic.

From this net dipole, all the piezoelectric properties of the ceramic arise. A piezoelectric ceramic is capable of developing an electric charge proportional to an applied mechanical stress. The degree to which the ceramic sample has been poled and the retention of this property during use over an extended period of time are of great importance if the ceramic material is to be used in a device. Unfortunately, a compromise must usually be made between ceramic compositions that are easily poled and compositions that retain a high degree of polarization when driven with high electric or acoustic fields.

The basic PZT ceramic is most often modified by the addition of small amounts of transition metal oxides in order to achieve either easy poling or a high degree of retention. Most studies of PZT have focused on how different additions in varying amounts affect the piezoelectric behavior of the ceramics.

The control of stoichiometry and the avoidance of additions of deliterious impurities during processing have been major problems which some earlier studies did not take into account.[1,2] Furthermore, differences in testing procedures (presumably) are responsible for the fact that reported results often are unreproducible by subsequent experimenters.[3,4]

The poling process used to produce previous results has typically been described by the conditions of poling: temperature, applied field, and time. As mentioned above, how thoroughly a sample is poled greatly affects its subsequent piezoelectric behavior. Usually it seems to be implied that if various samples are poled under identical conditions, they will yield piezoelectric ceramics with the same degree of polarization. The experiments carried out for this study test that assumption.

The experiments described here have been characterized by measuring the charge displaced during poling. This measurement is carried out on a large capacitor. The charge displaced is measured versus applied field at different poling temperatures. This makes evident the apparent saturation polarization for each sample and also at what applied field saturation occurs for each temperature. By determining the applied field at which that saturation occurs and plotting the log of that field versus the reciprocal of temperature, an activation energy type of plot should result. Measurements of piezoelectric coefficients will also be made to see how these correspond to the apparent saturation polarization observed.

## EXPERIMENTAL PROCEDURES

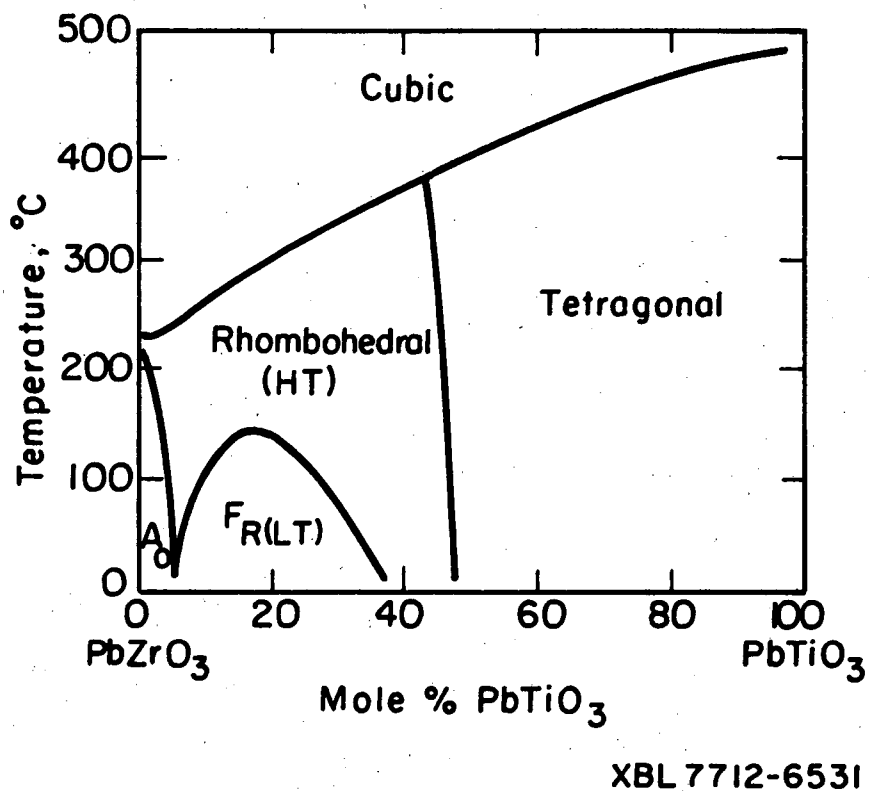
### A. Materials

The PZT investigated in this study consisted of four undoped compositions and two compositions modified with impurity additions. The undoped compositions had varied ratios of zirconia to titania. Compositions were: $Pb(Zr_{.58}Ti_{.42})O_3$, $Pb(Zr_{.52}Ti_{.48})O_3$, $Pb(Zr_{.50}Ti_{.50})O_3$ and $Pb(Zr_{.45}Ti_{.55})O_3$. These compositions were chosen to provide PZT with varying lattice types; rhombohedral, rhombohedral-tetragonal two phase boundary, rhombohedral-tetrogonal near the two phase boundary, and tetragonal lattices respectively, as shown by the phase diagram in Fig. 2. The doped compositions had additions of two atomic percent niobium and one and one-half atomic percent manganese, added as $Nb_2O_5$ and $MnO_2$. The additions were made before calcining to $Pb(Zr_{.52}Ti_{.48})O_3$. These additions are typical for use in a "soft" material (i.e. high piezoelectric coupling factor, low mechanical Q, high dielectric loss, etc.) and a "hard" material (i.e. high coercive field, low dielectric loss, high mechanical Q, etc.) respectively.[6] The change in properties is believed to arise from supression or generation of oxygen vacancies which affects whether 180° domains or 90° domains are formed.

Materials were prepared from high purity ($\geq$99.9%) reagent grade oxides according to the process outlined below.

### B. Processing

The starting oxides were carefully weighed and put in a latex-lined vibratory mill can. Zirconia milling media and isopropyl alcohol were used during the four hour milling.[9] The slurry was rinsed from the milling medium with isopropyl alcohol and put into a drying dish to be dried overnight in an oven at approximately 50°C. The dried powders were mixed




The $PbZrO_3$ - $PbTiO_3$ phase diagram.

Fig. 2

briefly by hand and packed into zirconia crucibles for calcining. Calcining was done at 850°C for 4 hours in air. The crucibles were covered with zirconia plates. After calcining, the slugs were crushed in a plastic bag with a lead mallet and sifted to less than 60 mesh. Polyvinyl alcohol (PVA) was added in the amount of 0.5 wt. % to aid in the formation of cold-pressed compacts by adding an appropriate volume of a 4 wt % solution of PVA in water. The PZT and PVA was put into a milling can again and 2.5 wt % excess PbO was added to enhance sintering of the PZT.[1] Approximately 400 ml $H_2O$ and 400 ml isopropyl alcohol were used with the zirconia media to mill this mixture as before for four hours. The water was added to the mixture to prevent the PVA from precipitating during milling. After milling, the mixture was slowly dried on a hot plate while it was mixed with a magnetic stirrer.

To prepare the dried powder for coldpressing, it was crushed and sifted through a 100 mesh screen. Approximately five grams of powder was pressed in a 1" steel die to 2,000 psi. It is essential to level out the powder carefully in the die before pressing, otherwise all areas of the powder will not be compacted evenly and cracking will result. No lubricant was used during pressing. Green density was calculated from the physical dimensions and found to be 60% theoretical.

Sintering was done at 1200°C for 8 hours in 1 atm $O_2$ obtained by evacuation and backfilling. A lead zirconate packing powder with 5 wt% zirconia was used to control stoichiometry at the sintering temperature.[1] The packing powder was mixed and calcined as previously described and passed through a 60 mesh sieve.

Approximately 2mm of packing powder was sifted onto the bottom of a 15 x 6 x 1.5cm$^3$ 99.5% alumina boat. The cold-pressed samples were

transferred into the boat and covered with packing powder. The boat was covered with a high density 99.8% alumina lid and placed in a horizontal Kanthal-wound alumina tube furnace. The furnace was cam driven at the rate of 300°C per hour to 1200°C, held for 8 hours, and allowed to cool in 10 hours.

Because all samples were somewhat warped after firing, they were ground flat by hand using 240 and then 400 grit silicon carbide on a glass plate. A special grinding holder was made for this purpose. It consisted of a 2"x 1/2" steel disk to which 1 mm of titanium carbide was cemented. A hole slightly larger in diameter than the fired samples was cut into the titanium carbide, to a depth of precisely 1 mm.

The wear-resistance of the face of this tool allowed each sample to be hand lapped easily to 1 mm + 0.03 mm. The use of 400 grit during the final portion of grinding insured a very sharp, well-defined edge. Water was used as a lubricant and carrier during the grinding.

Electrodes were applied by evaporating a layer of silver onto the surfaces of the sample in a standard vacuum evaporator. Lacquer was painted onto the edges to protect them from becoming metallized. The lacquer later was lifted off using acetone. This process produced electrodes which had no separation from the ceramic and extended in equal thickness to the very edge of each sample. The edge to edge resistance of the silver layer on a sample face was 2-3 ohms.

C. Materials Characterization

The crystal structure was determined by x-ray diffraction analysis of finely ground powders (<200 mesh) both after sintering and after firing. PZT was the only phase detected in all samples.

The apparent density was determined from dry and suspended weights in isopropyl alcohol relative to a nickel standard disk of approximately the same dimensions. The calculation used was:

$$\rho\text{sample} = \left(\frac{D_w}{D_w - S_w}\right)_{\text{sample}} X \left(\frac{D_w - S_w}{D_w}\right)_{\text{standard}} X\ \rho\text{standard}$$

where $\rho$sample = density of the sample

$D_w$ = dry weight

$S_w$ = weight suspended in liquid

$\rho$standard = density of standard, 8.91 gm/cc for Ni

This method does not depend upon the density of the liquid used, and variations due to temperature can be neglected. The theoretical density of PZT was taken as 7.98 gm/cc.

Grain size was determined from scanning electron and optical micrographs of polished and chemically etched surfaces using the line intercept method[11] and calculated from:

$$\text{Average G.S.} = \frac{L}{NM} X\ 1.5$$

where L = length of line on micrograph

N = number of grain boundary intercepts

M = magnification

D. Dielectric and Piezoelectric Measurements

Poling was done in a silicon oil bath. The oil was heated by means of a magnetically stirred hot plate and temperature measurements were made with a mercury thermometer immersed in the oil close to the sample. The hot plate was set at various temperatures for the different isothermal runs and held for a time such that the sample and oil bath could reach thermal equilibrium. The high voltage was applied across the sample by

means of an RF Oscillator with a maximum output of 5.7 KV. A motor-driven potentiometer was used to control the voltage output of a power supply which in turn was used to drive the high-voltage oscillator. The voltage across the sample was increased at the rate of 1.37 KV/min. past saturation polarization. The voltage was held constant while the sample was cooled to <40°C in the silicon oil. After the sample had cooled, the field was turned off and the sample was removed. The charge displaced during poling was collected on a 50 μF oil-filled capacitor in series as in a Saywer-Tower circuit.[12] The oil-filled capacitor was chosen for its low leakage. An electrometer was used to measure the voltage across the standard capacitor. The output from the electrometer was used to drive the y-axis of an x-y plotter. A voltage divider was used to determine the voltage applied and to drive the x-axis. The circuit is shown in Fig. 3.

The piezoelectric planar coupling coefficient $k_p$, and the mechanical quality factor, $Q_M$ were measured 24 hr after poling by the resonance method in accordance with I. R.E. standards.[13] The samples were driven at as low a field as was practical, typically 0.1 v/cm.[4] Values were calculated from

$$\frac{k_p^2}{1 - k_p^2} = 2.51 \frac{f_a - f_r}{f_a}$$

and

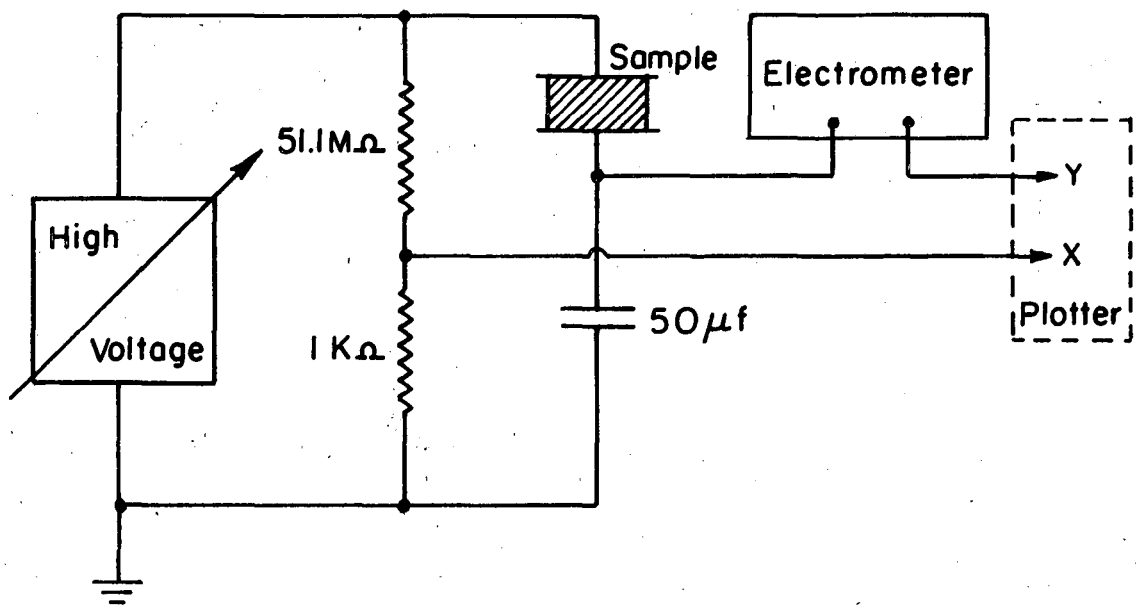
$$Q_M = f_a^2 \left[ 2\pi f_r R_r C \left( f_a^2 - f_r^2 \right) \right]^{-1}$$

where $f_a$ = anti-resonant frequency, HZ(maximum impedance)

$f_r$ = resonant frequency, HZ(minimum impedance)

$R_r$ = resistance at resonance

C = low field capacitance measured at 1 KHZ 24 hr after poling

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Poling circuit and instrumentation.

Fig. 3

The capacitance and dissipation factor at 1 KHZ were measured using a General Radio Corporation type 1650-A impedance bridge. The diameter-to-thickness ratio for the samples was >20:1 and a thin disk approximation was used in all calculations.

## RESULTS AND DISCUSSION

The measured apparent bulk density of all samples was >99% theoretical density. The excess PbO added to the composition after calcining aided the sintering by the formation of a PbO-rich liquid. Previous studies[1] have shown that this technique can be used without altering stoichiometry and results in a single final phase. X-ray diffraction patterns and scanning electron microscopy confirmed the presence of only a single phase in the samples used for this study. X-ray diffraction also confirmed that the composition $PZ_{.45}T_{.55}$ was well within the tetragonal region on the PZ-PT phase diagram (Fig. 2). From previous x-ray measurements[10] the calculated theoretical density of $PZ_{.5}T_{.5}$ was 7.98 gm/cc. The lattice constants were also determined to be: a = 4.040 Å, C = 4.129 Å.

The grain sizes are given in Table I. Although there is not much difference among the grain sizes for undoped PZT, the grains are noticeably smaller for the doped samples. The grain growth inhibition exhibited in the modified PZT relative to the unmodified PZT is similar to that shown by Atkin and Fulrath[8] in similar PZT compositions doped with $Nb_2O_5$ or $Al_2O_3$. These results indicate that a solute segregates at the grain boundaries and causes reduced grain boundary mobility. Both $Nb^{+5}$ and $Mn^{+4,+3}$ are believed to substitute for $Ti^{+4}$ in the perovskite lattice on the B site. The strongest argument for this postulate is that the sizes are favorable.

Some work has been done that suggests $Mn^{+n}$ might also substitute for lead on the A site.[14] Studies of the electrostatic potential in the perovskite structure predict that the valance which a manganese ion will assume is +4.[15] The characteristics of PZT doped with manganese, however, are similar to those of PZT doped with an ion which assumes a valence less than +4.

Table I. The average grain sizes of the compositions studied.

| SAMPLE COMPOSITION | AVERAGE GRAIN SIZE |
|---|---|
| $Pb(Zr_{0.58}\ Ti_{0.42})O_3$ | 3.8 μm |
| $Pb(Zr_{0.52}\ Ti_{0.48})O_3$ | 5.2 μm |
| $Pb(Zr_{0.50}\ Ti_{0.50})O_3$ | 4.8 μm |
| $Pb(Zr_{0.45}\ Ti_{0.55})O_3$ | 4.8 μm |
| $Pb(Zr_{0.52}\ Ti_{0.48})O_3$ + 1.5% Mn | 3.3 μm |
| $Pb(Zr_{0.52}\ Ti_{0.48})O_3$ + 2% Nb | 1.4 μm |

The $Nb^{+5}$ is a lead vacancy generator and the manganese acts as an oxygen vacancy generator. The type of ferroelectric domain structure formed upon firing is critically dependent upon the oxygen vacancy concentration. Ferroelectric domains can form in either 180° or 90° orientations. There is no strain energy associated with the 180° domains, but there is always some field energy. The mechanical energy required to form a 90° domain wall in a tetragonal lattice is much higher than that required to form a 180° domain wall due to the large mechanical strains associated with the (110) twins which form such walls. The 90° domains can close upon themselves entirely, head to tail, to yield a zero electric field energy.

The PZT lattice is cubic at high temperature and no polarization exists. Upon cooling through the Curie temperature (~380°C), the lattice goes through a displacive transformation to either a tetragonal or rhombohedral structure, depending upon the relative amounts of titania and zirconia. This phase change is accompanied by a spontaneous polarization. If the lattice is strained above the Curie temperature, formation of 90° domains may be favored on cooling through the Curie temperature to relieve these strains. Oxygen vacancies will have the greatest strains associated with them in the perovskite structure, and increasing the oxygen vacancy concentration will enhance the formation of 90° domains.

As the temperature is lowered farther below the Curie temperature, the tetragonal distortion increases and the strains accompanying the 90° domain walls become greater. The increased strain may be relieved by the diffusion of oxygen vacancies to the domain walls, effectively pinning the wall and creating a stable 90° domain which is difficult to switch. Any other position to which the domain wall is moved requires that the lattice

passes through an orientation of increased strain. This increase in strain will increase the energy of the system.

Suppression of oxygen vacancies by the addition of lead vacancy generators favors the formation of 180° domains. Differences in the domain structure have been observed on carefully etched samples of PZT made with different additives.[5]

After firing, the domain structure is randomly mixed to lower the electric field energy. Upon poling, domains aligned anti-parallel to the applied field will grow at the expense of the domains aligned with the applied field. When the field is removed, the domains which grew will leave the sample with a remnant net polarization.

An approximation of the maximum polarization achievable could be made in the following manner. Assuming a single crystal with a +4 B site ion whose direction of polarization would be (001), along the c-axis, the polarization is

$$P = \frac{Q}{A}$$

$$= \frac{(+4)(1.6 \times 10^{-19}\,\text{coul.})}{a^2}$$

For a = 4.04 Å, as in the PZT lattice,

$$P = 392\ \frac{\mu C}{cm^2}.$$

Since the domains are initially random, only half this polarization would be observed so that

$$P_{max} = 196\ \frac{\mu C}{cm^2}.$$

For a polycrystalline sample, this value would be lower due to ferroelectric domains which are not allowed to switch along the c-axis because the lattice orientations of the grains in which they are formed are unfavorable.

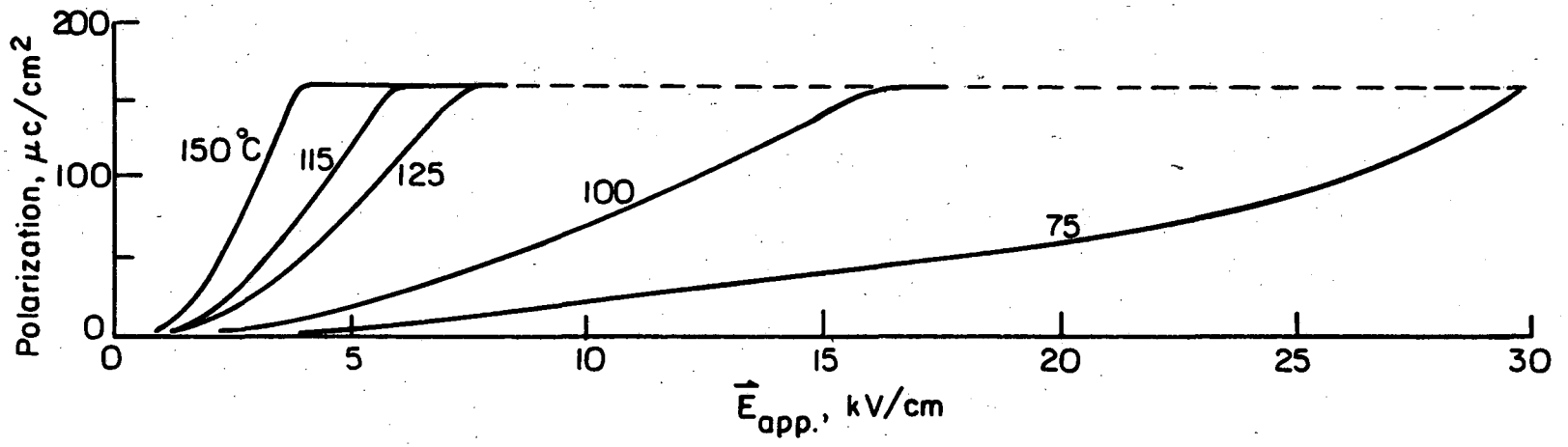
The poling curves for the different compositions of PZT are shown in Figs. 4 through 9. The values of the apparent saturation polarization for all compositions except PZT doped with niobium reach the same value of 161 $\frac{\mu C}{cm^2}$, which is 82% of the value estimated for a single crystal. The niobium doped samples reach an apparent saturization of about 34 $\frac{\mu C}{cm^2}$ at temperatures from 13°C to >100°C. At temperatures lower than 13°C, the apparent saturation polarization is 161 $\frac{\mu C}{cm^2}$.

Two other differences are evident in the poling curves for niobium doped samples. One difference is that the extent of domain switching is independent of temperature at temperatures greater than 13°C. The other is that the apparent polarization continues to show a slight but definite increase in magnitude after "saturation" has occurred. If this increase were due to an entirely dielectric effect, the relative dielectric constant in this high field region would be 11,700.

The coupling factor, $k_p$, and mechanical quality factor, $Q_m$, for the different compositions are summarized in Table II. There is no significant correlation among poling temperature, poling field and the magnitude of the piezoelectric doefficients within each composition. The values obtained compare favorably with previously reported values.[3,5,6,16]

The niobium doped samples had the highest coupling coefficient. This coefficient is generally regarded as the most representative measure of the degree of poling, yet it showed only a fraction of the apparent saturation polarization.

The remnant polarizationsof these samples must be higher than that of those doped with manganese or the undoped samples. This means that in the undoped PZT and PZT + Mn, most of the domain switching which occurs when

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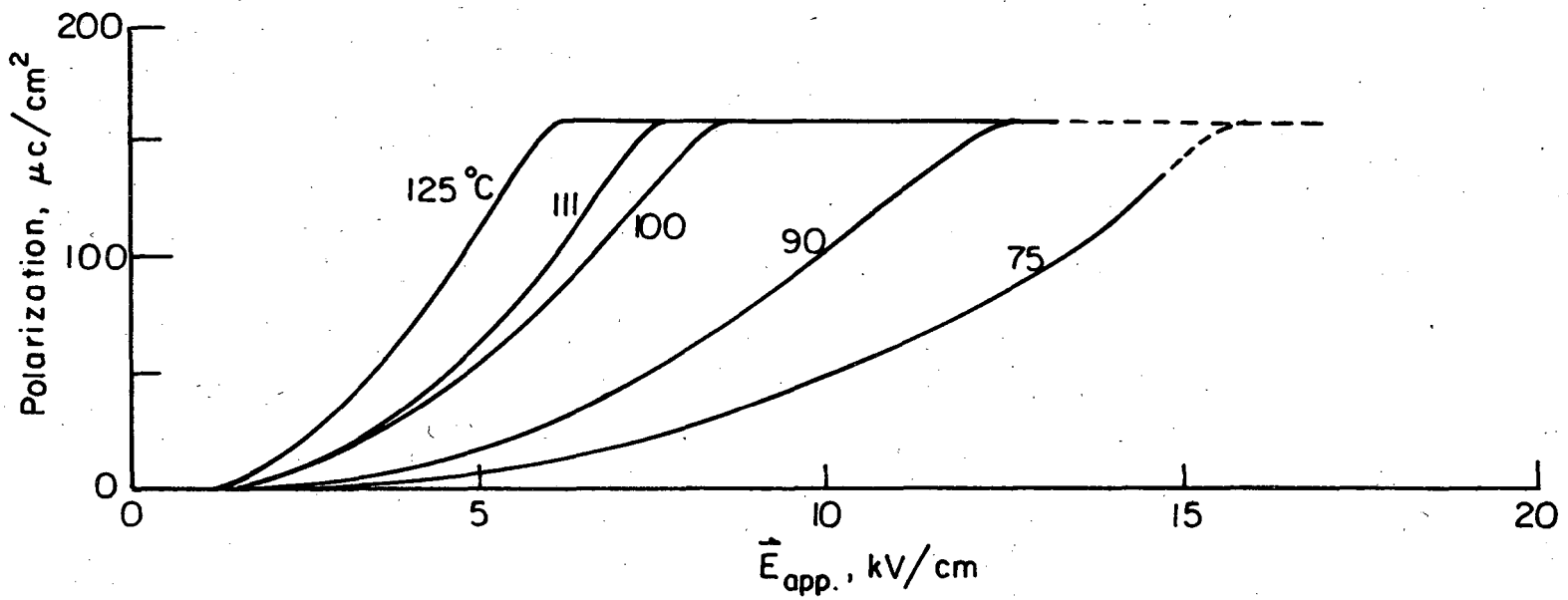
Polarization vs. applied field at various temperatures for $PZ_{.58}T_{.42}$.

Fig. 4

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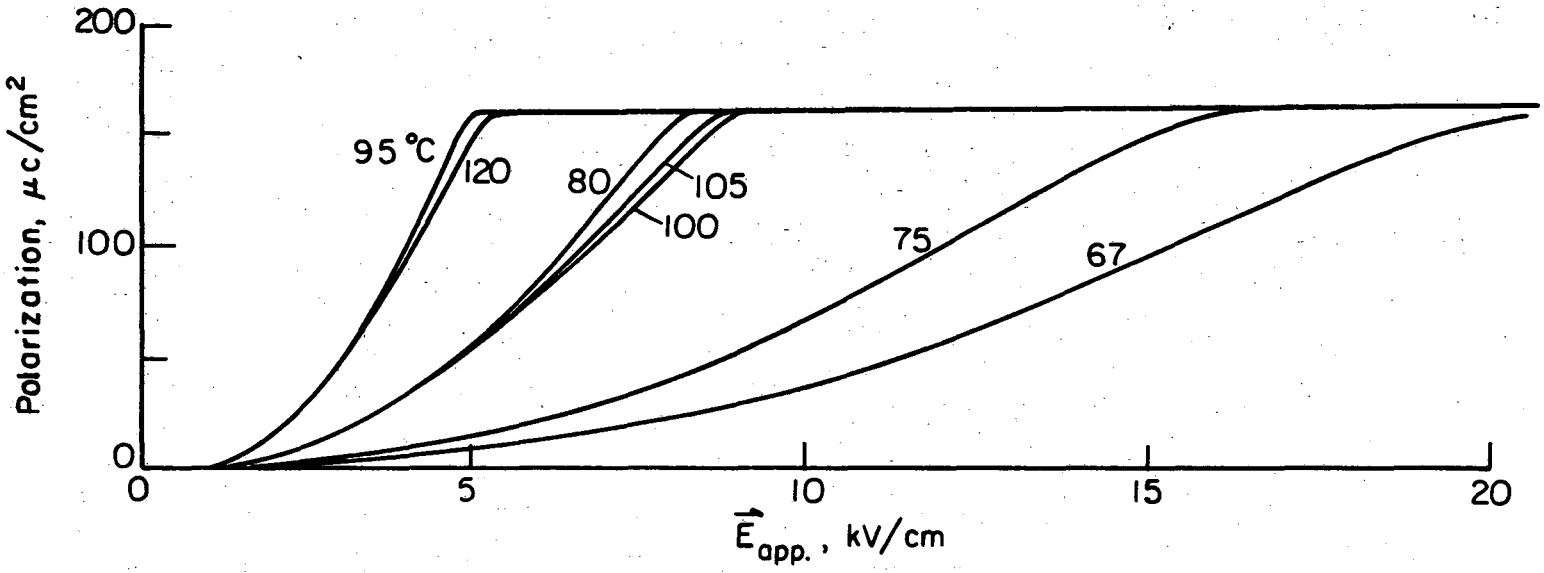
Polarization vs. applied field at various temperatures for $PZ_{.52}T_{.48}$.

Fig. 5

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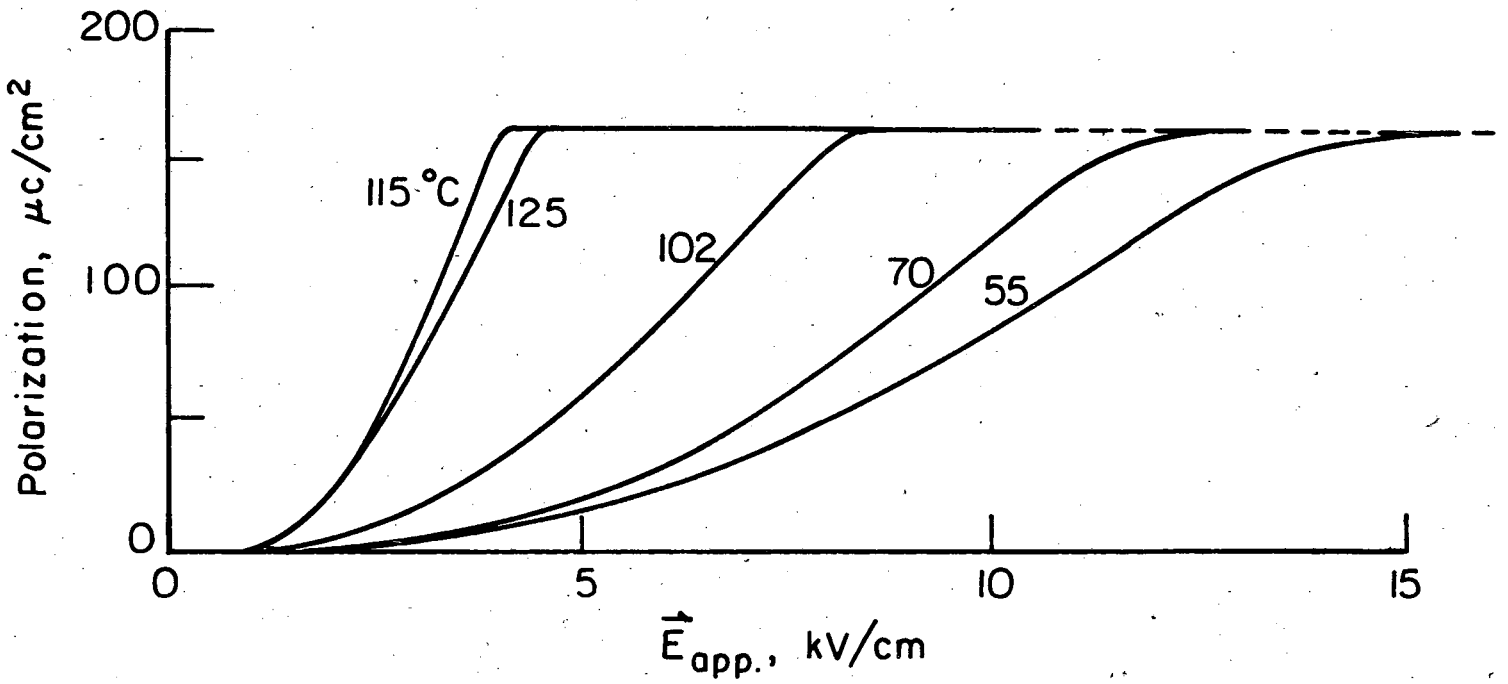
Polarization vs. applied field for various temperatures for $PZ_{.5}T_{.5}$.

Fig. 6

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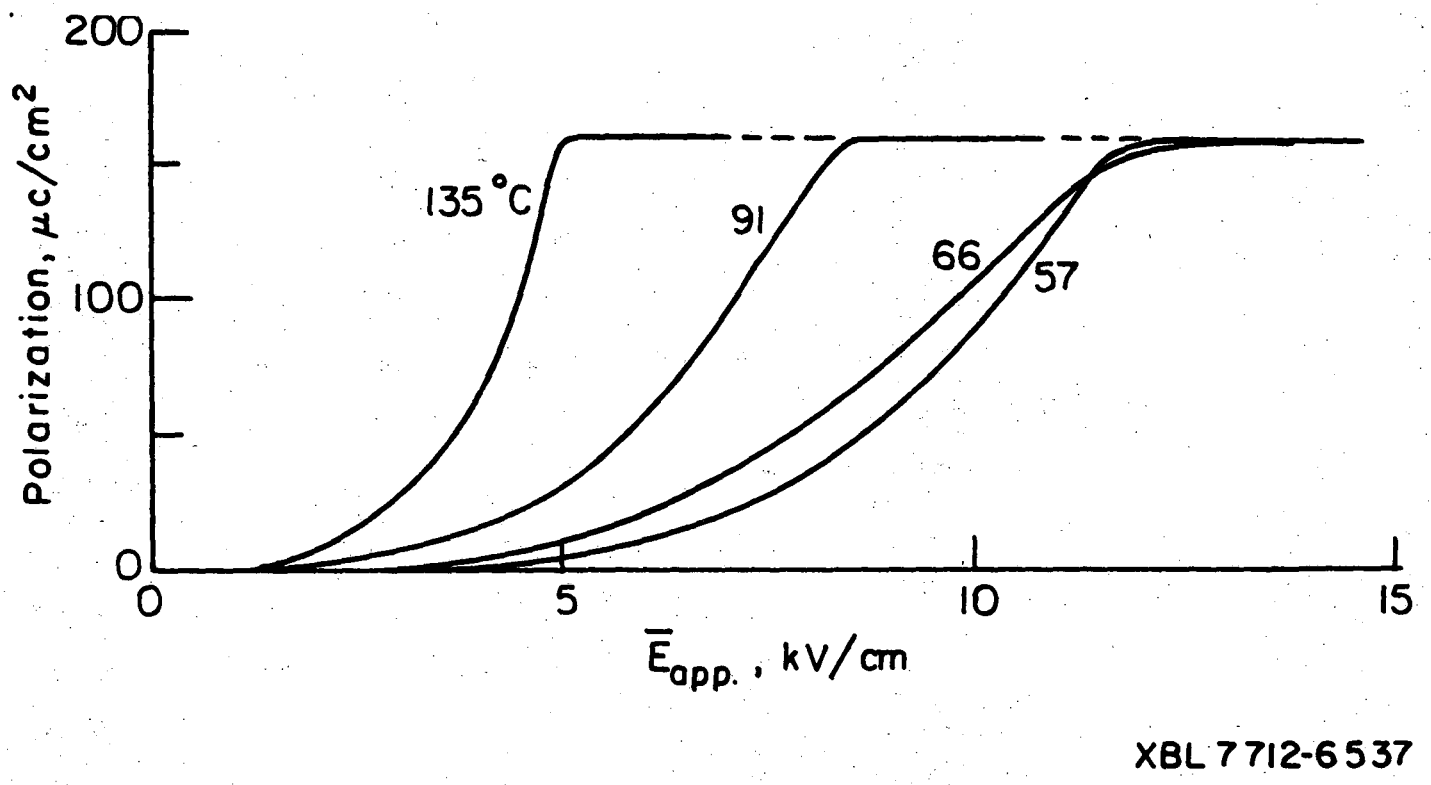
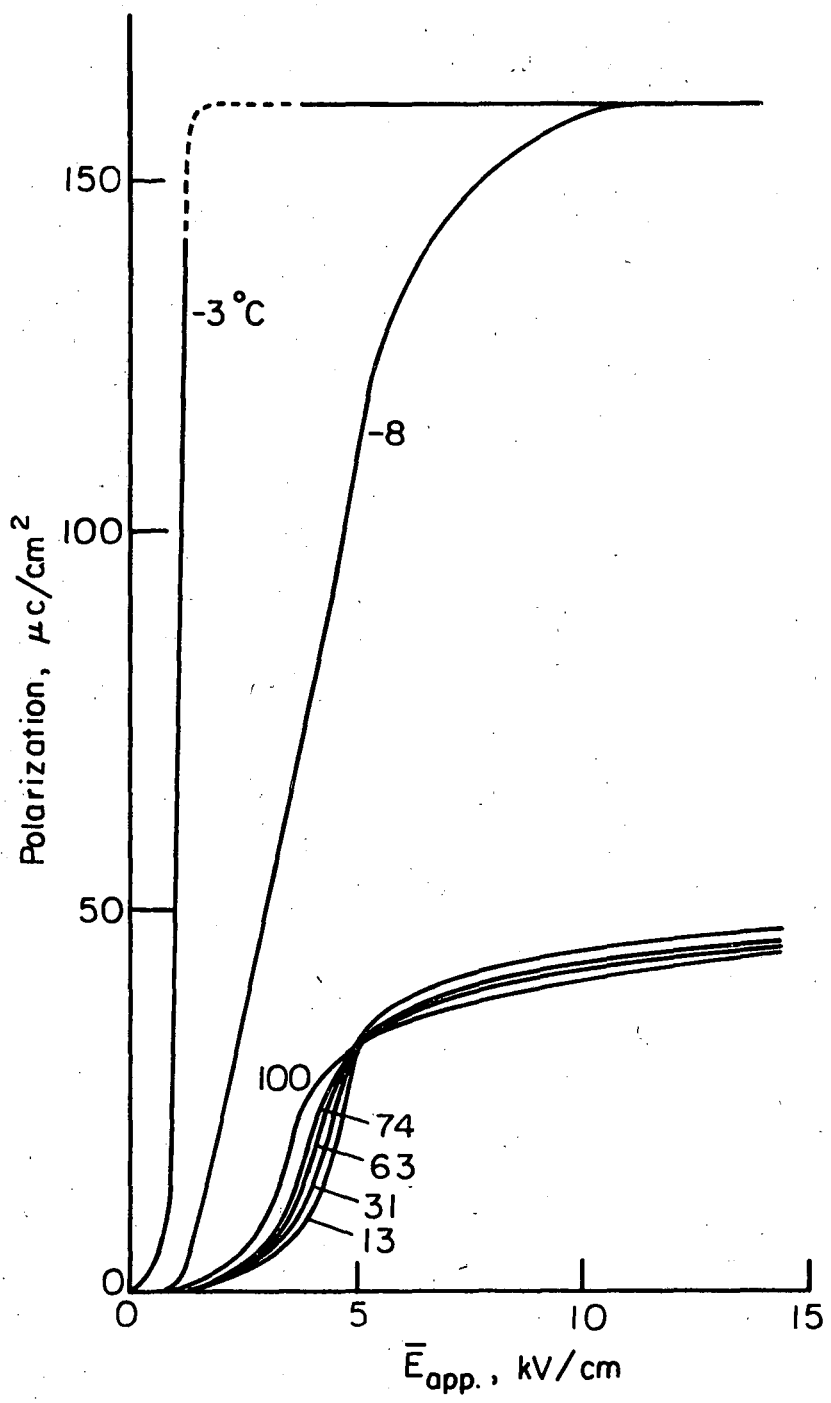
Polarization vs. applied field at various temperatures for $PZ_{.45}T_{.55}$.

Fig. 7




Polarization vs. applied field at various temperatures for $PZ_{.52}T_{.48}$ and 1.5% Mn.

Fig. 8

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Polarization vs. applied field at various temperatures for $PZ_{.52}T_{.48}$ + 2% Nb.

Fig. 9

Table II. Piezoelectric and dielectric properties of the lead zirconate-titanate compositions studied.

| Composition | Poling Temperature, °C | Planar Coupling Coefficient | Mechanical Quality Factor | Loss Tangent | Relative Dielectric Constant |
|---|---|---|---|---|---|
| $Pb(Zr_{0.58}Ti_{0.42})O_3$ | 75 | 0.180 | 379. | 0.015 | 559 |
| | 100 | 0.339 | 234. | 0.012 | 497 |
| | 115 | 0.228 | 245. | 0.009 | 943 |
| | 125 | 0.343 | 226. | 0.013 | 514 |
| | 150 | 0.358 | 261. | 0.013 | 463 |
| $Pb(Zr_{.52}Ti_{.48})O_3$ | 75 | 0.489 | 103. | 0.006 | 725 |
| | 90 | 0.499 | 94. | 0.008 | 863 |
| | 100 | 0.402 | 119. | 0.006 | 863 |
| | 111 | 0.500 | 105. | 0.006 | 787 |
| | 125 | 0.430 | 114. | 0.006 | 829 |
| $Pb(Zr_{.5}Ti_{.5})O_3$ | 67 | 0.329 | 133. | 0.006 | 877 |
| | 75 | 0.310 | 155. | 0.006 | 815 |
| | 80 | - | - | 0.005 | 556 |
| | 95 | - | - | 0.005 | 601 |
| | 100 | 0.199 | 136. | 0.006 | 812 |
| | 105 | 0.468 | 94. | 0.007 | 1019 |
| | 120 | 0.327 | 103. | 0.007 | 960 |
| $PB(Zr_{.45}Ti_{.55})O_3$ | 55 | - | - | 0.0045 | 577 |
| | 61 | - | - | 0.003 | 553 |
| | 70 | - | - | 0.003 | 542 |
| | 102 | 0.179 | 112. | 0.006 | 822 |
| | 115 | - | - | 0.005 | 563 |
| | 125 | 0.168 | 226. | 0.006 | 798 |
| $Pb(Zr_{.52}Ti_{.48})O_3$ + 1.5% Mn | 57 | 0.443 | 190. | 0.009 | 898 |
| | 66 | 0.474 | 154. | 0.010 | 760 |
| | 91 | 0.486 | 185. | 0.009 | 712 |
| | 135 | 0.482 | 223. | 0.006 | 743 |
| $Pb(Zr_{.52}Ti_{.48})O_3$ + 2% Nb | 8 | 0.509 | 43. | 0.021 | 1340 |
| | 10 | 0.521 | 49. | 0.020 | 1413 |
| | 13 | 0.520 | 38. | 0.020 | 1565 |
| | 31 | 0.530 | 35. | 0.020 | 1547 |
| | 63 | 0.537 | 46. | 0.020 | 1554 |
| | 65 | 0.545 | 39. | 0.020 | 1623 |
| | 74 | 0.549 | 45. | 0.022 | 1616 |
| | 100 | 0.542 | 37. | 0.022 | 1606 |
| | 117 | 0.529 | 38. | 0.020 | 1672 |

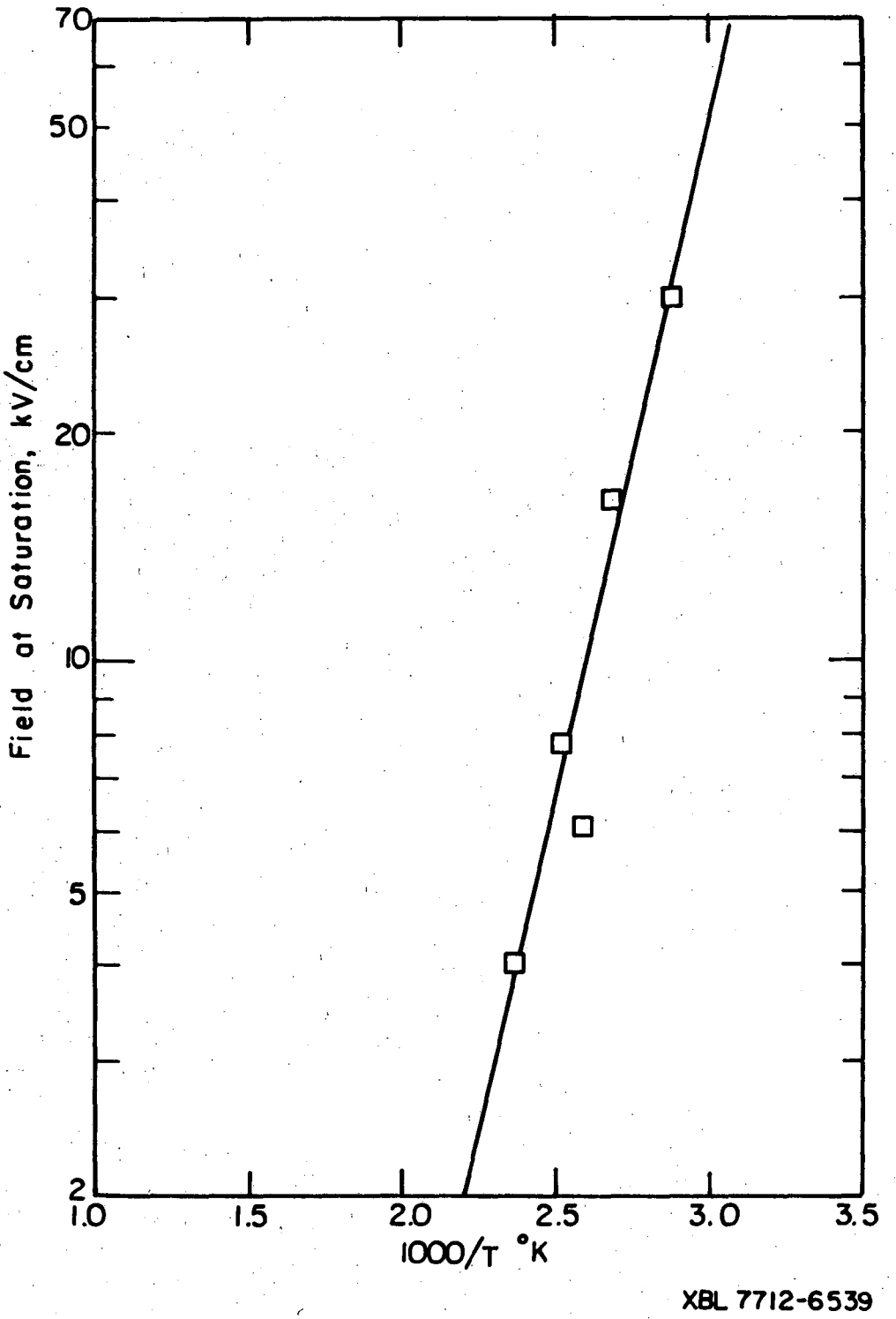
the high field is applied reverses to the original orientation after the field is removed.

Since the samples are not heated to the very high temperature required for solid state diffusion, the oxygen vacancies cannot migrate to the new 90° domain boundaries and relieve the lattice strain created when the walls moved. If the strain energy is sufficient, it will pull the domain wall back to its former low-energy position.

There is no strain energy associated with 180° domain switching, which is the switching shown by the niobium-doped samples. The niobium, by suppressing the oxygen vacancy concentration, causes a predominance of 180° domains to be formed. These domains remain switched after the field is removed but are easily realigned, resulting in the low $Q_M$ and poor aging characteristics of samples doped in this manner.[6,8]

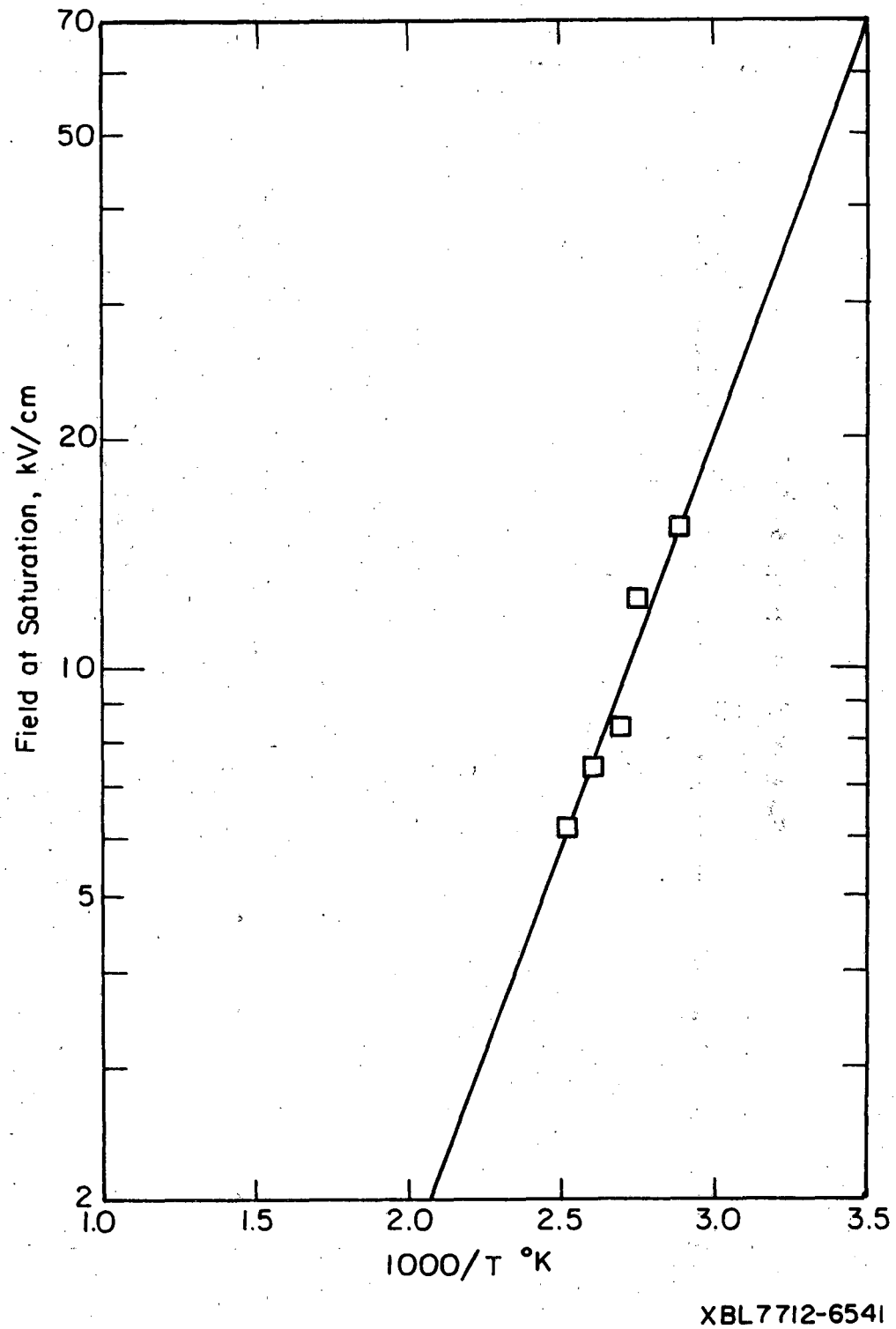
Plots of isothermal polarization versus applied field give the values of the minimum applied field which produces saturation for different temperatures. When these minimum fields for saturation are plotted versus 1000/T°K, as in Figs. 10 through 14, an activation energy type of plot results. From these curves it should be possible to predict the field required to produce maximum domain switching at temperatures below the Curie point. An increase in temperature gives the B site ion more kinetic energy to aid in switching. An increase in temperature also expands the lattice, lowering the energy barrier, which the B site ion must pass through in order to switch its unit cell dipole. A third effect of increasing the temperature is to lower the c/a ratio, which decreases the strain energy associated with 90° domain wall movement.

The observations that $k_p$ and $Q_n$ show no correlation to poling temperature suggest that, as long as the apparent saturation polarization



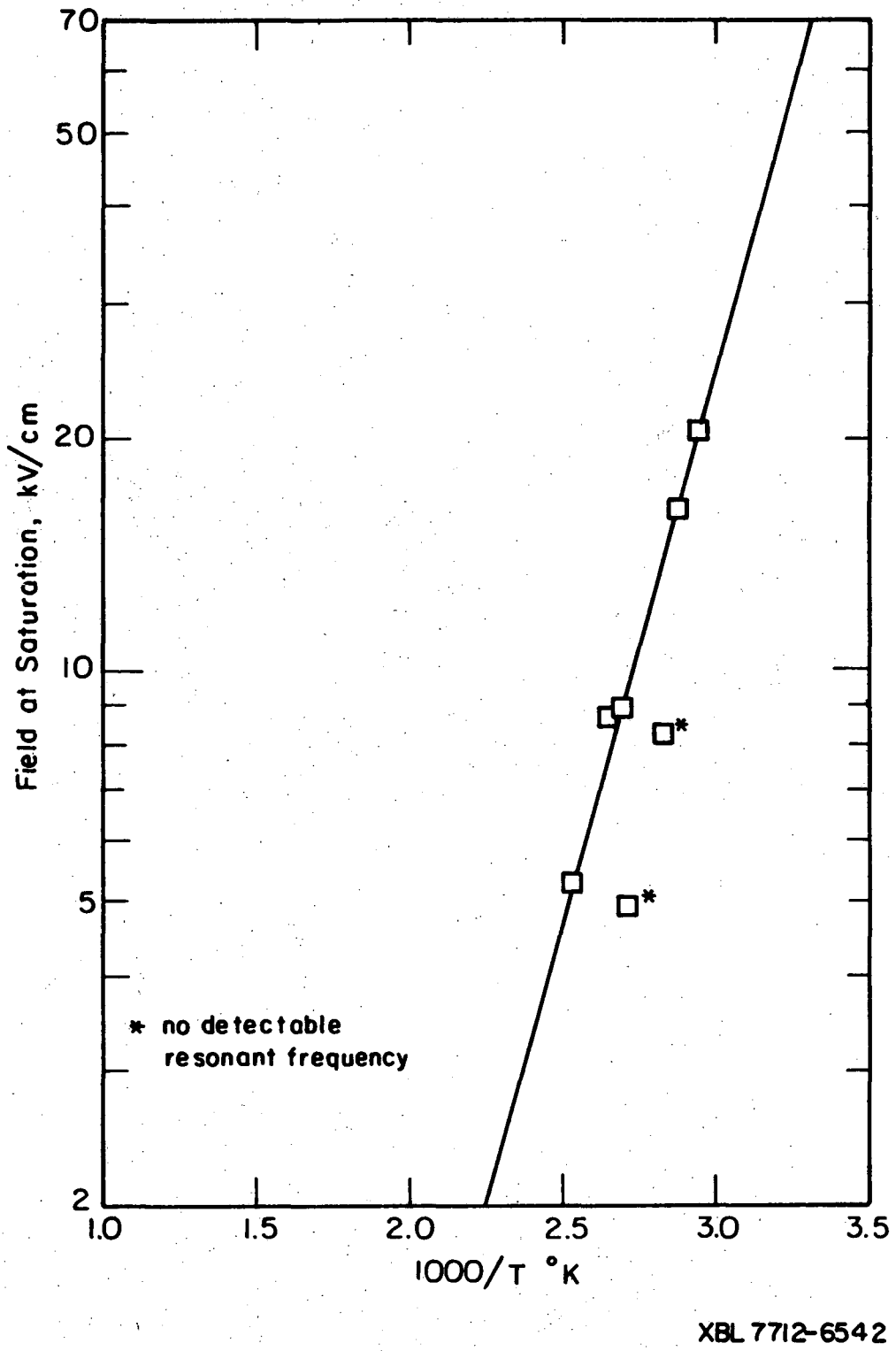

Field at saturation vs. 1000/T°K for $PZ_{.58}T_{.42}$.

Fig. 10



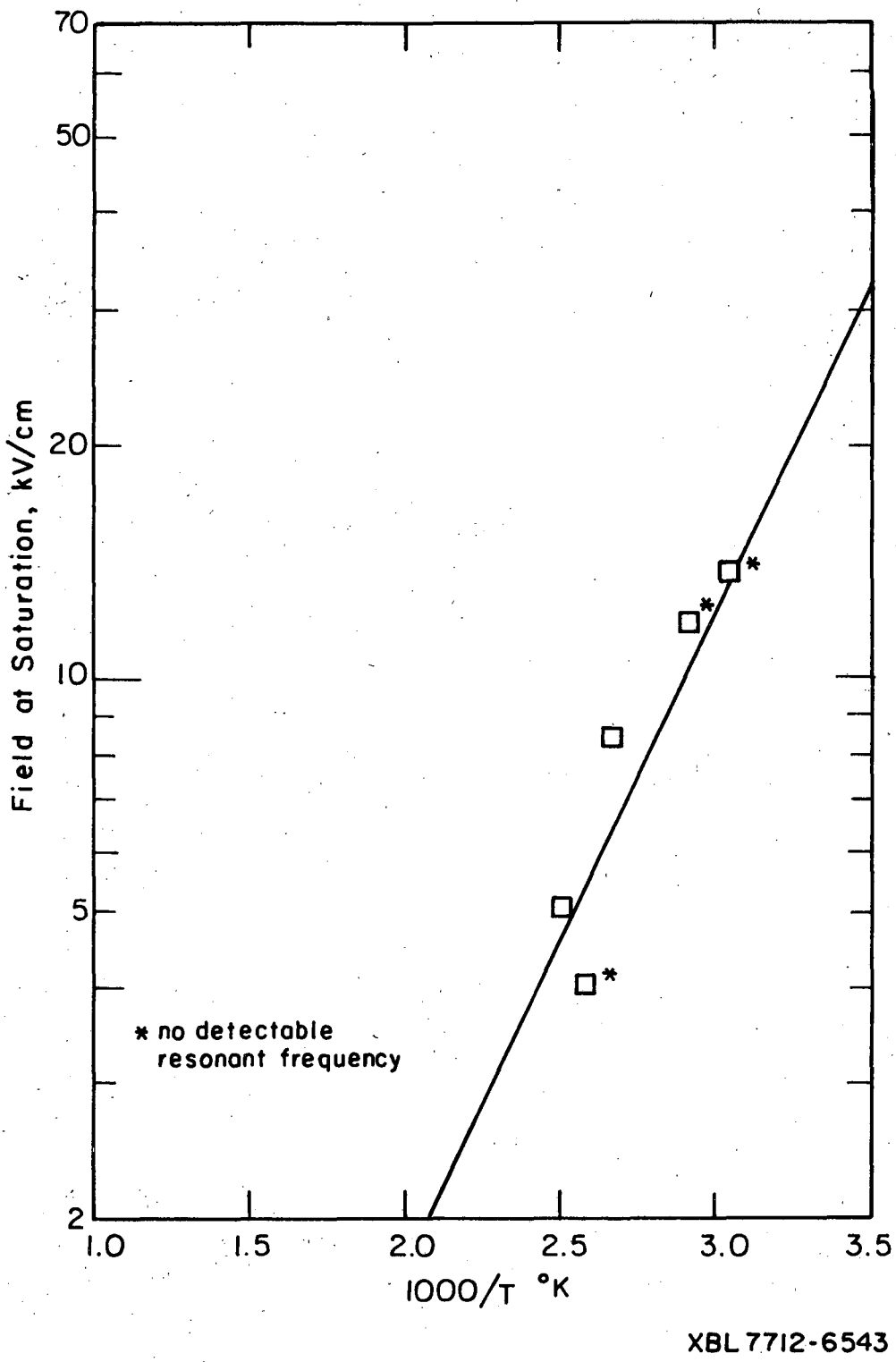

Field at saturation vs. 1000/T°K for $PZ_{.52}T_{.48}$.

Fig. 11



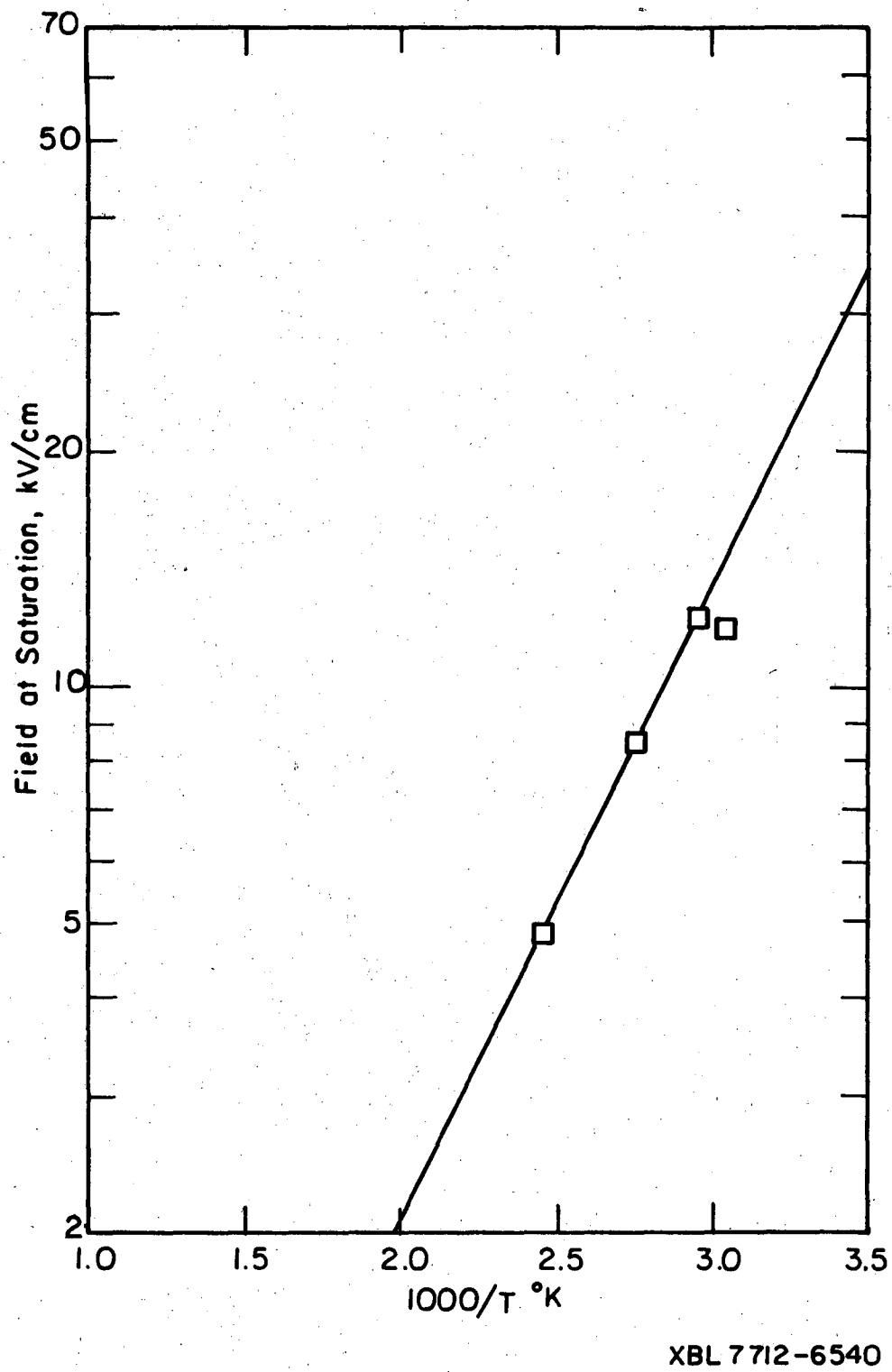

Field at saturation vs. 1000/T°K for $PZ_{.5}T_{.5}$.

Fig. 12




Field at saturation vs. 1000/T°K for $PZ_{.45}T_{.55}$.

Fig. 13




Field at saturation vs. 1000/T°K for $PZ_{.52}T_{.48}$ + 1.5% Mn.

Fig. 14

is reached, the piezoelectricity of poled PZT samples is independent of poling temperature if mechanisms such as oxygen vacancy diffusion are not available. Samples of the tetragonal composition ($PZ._{45}T_{.55}$) often cracked upon firing. The displacive shear transformation which occurs upon cooling through the Curie temperature may have caused this cracking. Residual stresses may exist in some specimens of this composition which didn't crack. No piezoelectric behavior was detectible in some of these specimens even though an apparent saturation polarization was observed. Residual lattice strain may be responsible for prohibiting any permanent polarization from occurring.

Comparison of the piezoelectric coefficients with the polarization curves indicates that the apparent saturation polarization is not the significant property to consider. The remnant polarization is a much more meaningful prediction of piezoelectric behavior. Measurement of the remnant polarization would not be accurate with this experimental set-up because of the medium used for poling. The silicon oil was carefully filtered to remove dust and other particles before poling, but even so, charged particles undoubtably exist in the oil. Any dielectric breakdown through the oil would also create charges. These charges would migrate onto the faces of the sample to reduce the net energy. As the applied field was removed, these charges would be released from the surface and the large standard capacitor could not discharge back through the sample. The decrease in polarization measured is the decrease in charge across the standard capacitor. The actual decrease in polarization is reflected by both the amount of charge displaced from the sample faces into the silicon oil and the charge which flows from the standard capacitor back onto the sample.

## CONCLUSIONS

The electrical properties of PZT are dependent primarily upon its composition. The trends of $k_p$ and $Q_M$ with composition determined in this study compare favorably with previously reported values.[3,5,6,16] There is no significant variation of piezoelectric coefficients for samples poled at temperatures in the range of 60°C to 100°C, although increases in the coefficients might be obtained if the poling field were held for a long enough time at an elevated temperature to allow the migration of oxygen vacancies.

The remnant polarization is only a fraction, probably less than 20%, of the saturation polarization. If a poling process could be devised to increase the remnant polarization, greatly increased coupling coefficients could be expected. Increasing this polarization in a material with a typically higher mechanical quality factor would yield a generally superior piezoelectric material. Such characteristics of a material as grain size and residual stresses can also affect how a material poles and its subsequent behavior; therefore, merely poling several samples under identical conditions does not guarantee uniformly poled samples.

The applied field required for saturation polarization at a given temperature can be estimated from data generated by measuring the field at saturation for various temperatures, as shown in Figs. 10 through 14. Extrapolations of this plot show that for most compositions, saturation polarization is impossible at room temperature because the field required is greater than the dielectric breakdown strength of the material.

Dielectric breakdown usually occurs below the expected field strength through pores which act as a distributed dielectric with a much lower dielectric permittivity and strength than the ceramic. If the samples are

very dense, breakdown through the pores can be avoided, but breakdown then is most likely to occur through the poling medium down the edge of the sample.

## ACKNOWLEDGMENT

I am deeply indebted to the late Professor R. M. Fulrath for the inspiration and guidance he gave me. I would also like to express my thanks to Professors R. S. Muller and A. W. Searcy for their invaluable suggestions and counsel, and Professor R. M. White for his help in editing this manuscript.

This work was supported by the Division of Basic Energy Sciences, U.S. Department of Energy.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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