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SINTERING Sc AND Nb MODIFIED LEAD ZIRCONATE TITANATE

Douglas Christopher Lee
(M. S. Thesis)

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SINTERING Sc AND Nb MODIFIED LEAD ZIRCONATE TITANATE

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SINTERING Sc AND Nb MODIFIED LEAD ZIRCONATE TITANATE

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ABSTRACT

The $\text{Pb}(\text{Zr}_{.53}\text{Ti}_{.47})\text{O}_3$ system was doped with niobium and scandium ions to correlate sintering behavior and ferroelectric properties to a proposed lead vacancy model. Compositions of 1.5 at.% Nb, 1.5 at.% Nb-1.5 at.% Sc, and 1.5 at.% Nb-3.0 at.% Sc were sintered at 1150°C, 1200°C, and 1300°C and densification and grain growth data were tabulated.

Weight loss data, microprobe analysis, X-ray diffraction and ferroelectric hysteresis loops were used to characterize the system. Evidence supporting a low solubility limit of scandium in the lead zirconate titanate system was presented. The suppression of sintering and ferroelectric properties by the addition of scandium to lead zirconate titanate and the enhancement of these properties by niobium strengthens the proposed lead vacancy model.

I. INTRODUCTION

Lead zirconate titanate has received considerable attention in recent years for its electronic applications. Economic considerations preclude the use of this material in many applications, yet the constituents in their powder form and correct impurity content are relatively inexpensive. The high cost is due to the difficulty in ceramic processing. Electrical properties are not reproducible because of uncontrolled parameters in ceramic processing. The purpose of this study was to determine the actual phenomenon and mechanisms encountered in ceramic processing and sintering of lead zirconate titanate. The results should lead to improvement of the reproducibility and reliability of electrical properties of this material.

The work that has been done on this system is mainly of an engineering nature directed toward optimizing ferroelectric and piezoelectric properties and not concerned with understanding actual mechanisms involved. This is understandable due to the complexity of manufacturing processes and parameters.

The theoretical single crystal models derived by physicists and the results of data obtained by researchers using polycrystalline samples are very difficult to correlate in terms of dopants and their effect on electrical properties. Static models, dynamic models based on lattice dynamics, and the phenomenological thermodynamic theories all dealing with single crystals do not account for compositional variations.¹ Polycrystalline models are no better in this respect.

It is possible to propose a lead vacancy model using the current "state of the art" ceramic technology to relate dopant concentrations to

lead vacancy concentration and sintering behavior in lead zirconate titanate. The shape of ferroelectric hysteresis loops seems to have a strong relation to proposed lead vacancy concentrations. This can be deduced from observing experimental data and may be used to aid in understanding sintering results.² Experiments that could relate conclusively the proposed lead vacancy model to actual behavior would be beneficial.

Proposed Mechanism of Sintering Lead Zirconate Titanate

Sintering is increasing the strength and/or density of a particulate compact by application of a relative high temperature with the reduction of surface free energy as the driving force. Kingery gives four basic mechanisms by which sintering a single phase material may take place: surface diffusion, evaporation condensation, volume diffusion, and viscous flow.³ The degree to which any one mechanism predominates depends upon the material and temperature. Only the latter two mechanisms result in densification. In the lead zirconate titanate system, the governing mechanism appears to be volume diffusion or grain boundary diffusion,² both of which have essentially the same atomistic mechanism of mass transport.

An indication of sintering behavior in this system in relation to dopants may be obtained by examining ferroelectric hysteresis loops of differently doped material. Atkin showed a relation between the lead vacancy concentration and the type of hysteresis loop observed in lead zirconate titanate.²

The structure of lead zirconate titanate above the Curie temperature is the perovskite type with 8 Pb^{2+} ions on the corner sites, Zr^{4+} and Ti^{4+} occupying the center site, and O^{2-} in the 6 face centered sites.

The structure and a table of ionic radii are shown in Fig. 1 and Table I, respectively.^{4,5}

Table I. Ionic Radii

<u>Ion</u>	<u>Ionic Radii in Å</u>
Pb ²⁺	1.20
Zr ⁴⁺	0.79
Ti ⁴⁺	0.68
Sc ³⁺	0.81
Nb ⁵⁺	0.69
O ²⁻	1.40

The volume diffusion mechanism in this system has four ionic diffusivities associated with it, one for each different ion. The slowest one of these diffusivities will be rate controlling. A first approximation method of determining which cation would be the slowest moving specie is to examine single bond strengths of the component oxides determined from the dissociation energy per gram atom of oxygen divided by the coordination number of the oxide. The zirconium ion and titanium ion have 81 kcal/mole and 73 kcal/mole, respectively, for single bond strengths with 6 fold coordination, while the lead ion has 12 kcal/mole with 12 fold coordination;⁶ thus the zirconium ion should have the lowest diffusivity. Anions are not thought to be the slowest moving specie because of the insensitivity during sintering of the lead zirconate titanate system to different partial pressures of oxygen.⁷ The ionic

size, ionic charge and ionic coordination further substantiate designating the zirconium ion as the slowest moving specie in this system.

Coble's equation for second and final stage sintering may be written in the form⁸

$$\frac{dP}{dt} = \frac{ND\gamma\Omega}{\ell^3 kT}$$

ℓ = grain size

P = Porosity

N = geometry factor

D = diffusivity of slowest moving specie

Ω = vacancy volume

γ = surface energy

and shows that the rate of sintering may be enhanced by optimizing grain size, diffusivity and temperature. The high vapor pressure of lead oxide over the system at sintering temperatures results in severe limitations in increasing firing temperature; thus, to make sintering a practical fabrication process for this material, dopants must be added to stop discontinuous grain growth, to increase the diffusivity of the slowest moving specie, and also to be beneficial to the desired electrical properties of the system.

Burke shows that stopping discontinuous grain growth in aluminum oxide is important if theoretical density is desired.⁹ The pores must remain on the grain boundaries for theoretical density to be approached; thus, if a grain boundary breaks away from a pore so that the pore is left in the interior of the grain, the pore will close at a very slow

rate due to increased diffusion path lengths. Coble, Jorgensen, and Burke¹⁰ separately concluded that magnesium oxide added to aluminum oxide prevented secondary grain growth but did not prevent normal grain growth. Burke explains this as reduction of grain boundary mobility by the addition of a solute.¹⁰ Coble's equation also predicts that the rate of densification is inversely proportional to the grain size cubed; thus, the densification rate is very sensitive to any increase in grain size.

Further consideration must be given to the dopant with respect to its effect on the diffusivity of the slowest moving specie of the system. In order for a zirconia ion located on a B site to jump from one unit cell to an adjoining unit cell, the adjoining unit cell must be vacant. Also, being a highly charged ion, electrostatic repulsion will prevent it from approaching a charged lead ion. It may be postulated that for a zirconia ion to jump, the path that would require the lowest energy would be through a vacant lead ion site and into a vacant adjoining B site. Interstitial models and oxygen vacancy models are possibilities but seem unlikely from observing the experimental results from the system. Pryor showed that the oxygen pressure had no effect on the densification rate of the system except to allow 3% higher end point densities due to the presence of a diffusible gaseous specie entrapped in the pores.⁷ Holman's weight loss experiments indicate the presence of extrinsic lead vacancies also.¹¹ This leads to postulating that lead vacancy concentration may be directly proportional to the diffusivity of the slowest moving specie.

The lead vacancy concentration may be controlled by small additions of dopants with a unit variation of ionic charge and with the ionic radius suitable for ionic substitution. Atkin showed in this system that aluminum oxide had a measurable solubility even though it has an ionic radii of .51, which is 25% smaller than titanium and violates previous crystal chemistry rules of solubility.¹² The model results in one lead vacancy for every two ions of plus five charge incorporated on a zirconia or titania site which has a charge of four. Also, suppression of intrinsic lead vacancies is possible by placing a plus three charge ion on the zirconia and titania site. The two ions chosen for this were Nb⁵⁺ and Sc³⁺ which have ionic radii of .69 Å and .81 Å, respectively. It was thought that both ions added in quantities below the solubility would inhibit grain growth and niobium would increase the diffusivity of the slowest moving specie, thereby enhancing the rate of densification. Originally an analysis of isothermal sintering curves was proposed for three different scandium and niobium doped compositions with the hope that Coble's equation could be applied to determine relative diffusivities and activation energies. The suppression of the rate of densification by the addition of scandia ion to lead zirconate titanate was so great that complete data for an in-depth analysis could not be obtained. Thus, the results will be treated in a qualitative manner.

The solid solution system of $Pb (Sc_{.5}Nb_{.5})_{1-x}M_xO_3$, where M is a zirconium, titanium or hafnium ion, have been studied by Tennery, Hang, and Novak,¹³ and also by Johnson, Valenta, Dougherty, Douglass, and Meadows.¹⁴ Both directed their research toward trends in electrical properties with varying composition.

II. EXPERIMENTAL PROCEDURE

The titania, zirconia, lead oxide, and calcined powders used in this investigation were analyzed by semi-quantitative analysis to determine their impurity content. The calcined powders showed a maximum of 300 parts per million for any one impurity whereas dopant levels were greater than 3000 parts per million. The results of this analysis are given in Table II.

Table II. Analysis of Raw Materials *

<u>T.G.A. Titania Titanium Corp. of America</u>		<u>Reactor Grade Zirconia Wah Change Co.</u>		<u>Reagent Grade PbO Baker Chemical</u>	
Pb	300 ppm	Ti	60 ppm	Ti	20 ppm
Si	600 ppm	Ba	<100 ppm	Ba	10 ppm
Mg	30 ppm	Mn	< 10 ppm	Si	20 ppm
Fe	<20 ppm	Si	500 ppm	Mg	10 ppm
Ca	70 ppm	Hf	2500 ppm	Ag	5 ppm
Al	400 ppm	Mg	100 ppm	Ca	10 ppm
		Fe	300 ppm	Bi	300 ppm
		Ca	150 ppm	C	5 ppm
		Cr	<100 ppm	Al	10 ppm
		Co	< 30 ppm		

Analysis of Nb Doped Lead Zirconate Titanate
Plus Scandium Oxide Titrated Additions.

	<u>1.5 at.% Nb</u>	<u>1.5 at.% Nb- 1.5 at.% Sc</u>	<u>1.5 at.% Nb- 3.0 at.% Sc</u>
Nb	7000 ppm	7000 ppm	5000 ppm
Sc	50 ppm	2500 ppm	7000 ppm
Si	100 ppm	100 ppm	100 ppm
Al	300 ppm	300 ppm	250 ppm
Mg	40 ppm	30 ppm	40 ppm
Ca	200 ppm	200 ppm	200 ppm
(Theoret. Nb doping level)	Nb 6100 ppm Sc 0 ppm	6100 ppm 3200 ppm	6100 ppm 6400 ppm

* Semi-Quantitative Spectrographic Analysis; parts per million of the oxide of the element shown by weight.

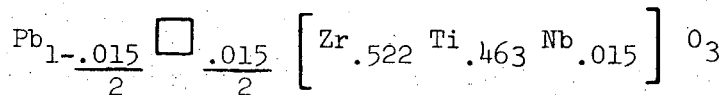
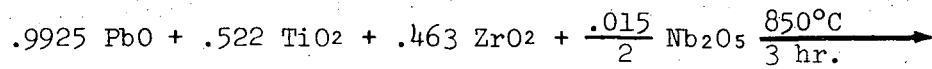
Powders were dried at 110°C to remove the absorbed water and weighed. Twelve mole batches were loaded into a 1.5 gallon rubber lined ball mill. The 53-47 ratio of zirconia to titania was chosen because of the optimization of electrical properties due to a low temperature phase boundary near this composition. Teflon media and a rubber lined ball mill minimized contamination during mixing. The batch was wet mixed with isopropyl alcohol for fifty hours and dried at 79°C. Additional dry mixing was done for five hours.

Slugs were isostatically pressed at 30,000 pounds per square inch using rubber tubing for molds. The slugs were inserted into a platinum crucible and calcined for three hours at 850°C and air quenched. The proposed reaction is given in Table III. The niobium dopant was added before mixing of the oxides because it is not available as a soluble salt, which makes it difficult to add to the material homogeneously; it enhanced the kinetics of the calcining reaction. Data from calcining experiments indicates that pure lead zirconate titanate is not fully reacted at 850°C for 24 hours while 1.5 at.% Nb doped material shows no X-ray diffraction evidence of the oxides after 3 hours. It was necessary to give the powders the same treatment until after calcining and grinding to insure uniform particle size and completion of the calcining reaction. The calcining time versus particle size was measured to obtain the shortest time in which the oxides are fully reacted and have the smallest particle size. The average particle size was measured with a Fisher Sub-sieve sizer.

The calcined slugs of the 12 mole batch of 1.5 at.% niobium doped lead zirconate titanate material were crushed in a lucite automatic

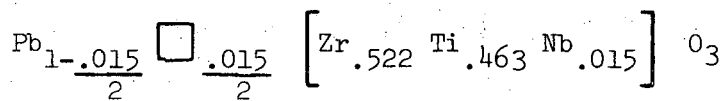
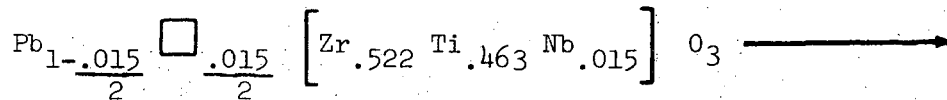
Table III. Postulated Reactions

Calcining

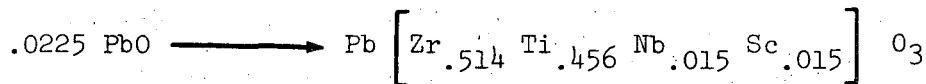
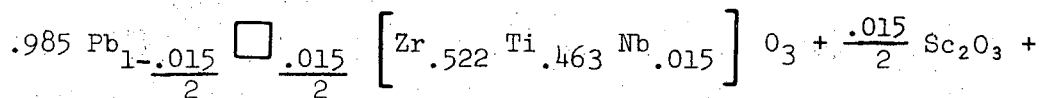


Sintering

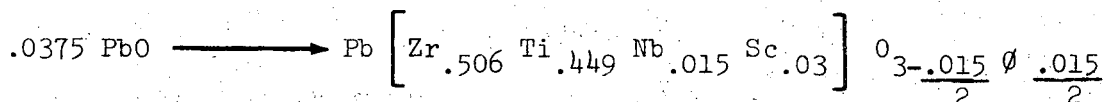
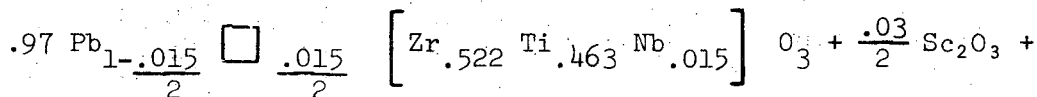
1.5 at.% Nb



01.5 at.% Nb 1.5 at.% Sc



1.5 at.% Nb 3.0 at.% Sc



Where \square indicates a lead vacancy and \emptyset indicates an oxygen vacancy.

mortar and pestle for ten minutes. Grinding was done with a "Sweco" vibratory mill using a polyurathane liner and lucite media to minimize contamination.

A variation of technique was to wet vibratory mill 500 grams of the 12 mole batch with zirconia media. The 500 grams were mixed with the larger batch and proved a source of 20 micron zirconia particles subsequently observed in the microstructure. Dry vibratory milling with lucite media was found to be the most effective in obtaining average particle size of $1.5\mu\text{m}$ with minimum contamination and all but 500 grams were milled in this manner. A 500 gram batch was milled ten hours using this technique and particle sizes were measured with a Fisher Sub-sieve sizer and a scanning electron microscope; the latter showed a particle size range of approximately $.25\mu\text{m}$ to $3\mu\text{m}$. The lucite contamination obtained from abrading the grinding media was removed by heating the powder to 450°C for 24 hours.

The 12 moles of 1.5 at.% niobium doped lead zirconate were divided into three equal quantities, and scandium and lead oxide were added using titration techniques with nitrate solutions. One batch received no additions and remained as 1.5 at.% niobium doped lead zirconate titanate. The second had 1.5 mol.% scandium nitrate and .225 mol.% of lead nitrate titrated, while the third had 3.0 mol.% scandium nitrate and 3.0 mol.% lead nitrate titrated.

The slurry formed in titration was stirred magnetically while being evaporated to coat each grain of the lead zirconate titanate with an appropriate layer of precipitated dopant. The nitrates were oxidized at 450°C for 12 hours. The dopants were added after calcining to insure

that the average particle size and distribution were uniform between the three differently doped materials so as not to affect the validity of sintering data obtained.

The results of a semi-quantitative spectrographic analysis are given in Table II along with the calculated doping levels. Reasonable agreement is shown considering the $\pm 50\%$ accuracy of the spectrographic analysis. To improve the cold pressing characteristics, 10 cm³ of isopropyl alcohol were added to each 900 gram batch. The powders were stored in desiccators with equilibrium vapor pressure of isopropyl alcohol to prevent evaporation.

Cold pressing of the powders was done in a 3/4 inch die of a tungsten steel alloy at 18,000 p.s.i. The pellets ranged in weight from 6 to 9 grams and had enough green strength to allow removal of the contamination caused by the die wall. The green densities were 63% theoretical density for the 3 different compositions.

The pellets were sintered in cylindrical 10 mil platinum crucibles with covers. The high vapor pressure of lead oxide necessitated the use of packing powder techniques to provide a lead vapor surrounding the pellets. The dopants in the pellets have a definite effect on the activity of lead oxide in the pellets compared to the activity of the undoped packing powder, although in this experiment this was not taken into account. The packing powder was left in a coarse agglomerated form to facilitate removal of the pellets after sintering.

A kanthal wound atmosphere furnace was used for sintering the pellets. The furnace was pumped down for 45 minutes to about 100 μ m with a fore pump; then a flowing oxygen atmosphere was introduced. The thermal

gradient in the hot zone was less than $\pm 5^{\circ}\text{C}$ and the heating rate was 20°C per minute. The specimens were partially quenched by removing the crucible to a temperature zone of about 800°C . This quench lowered the temperature so that sintering could not take place but prevented the specimens from being thermally shocked.

The postulated calcining and sintering reactions are given in Table III. The weight change upon sintering was recorded as a check on the postulated reactions. Also, microprobe analysis, X-ray diffraction, and ferroelectric hysteresis loops were used to indicate whether the predicted reactions were correct and if not, the actual reactions that were taking place.

A microprobe examination of sintered pellets of each of the three different compositions was done as a check on the postulated reactions given in Table III. Samples of each composition with the largest grain size and highest density were polished and coated with a conductive layer of carbon. Corresponding areas of each sample were scanned and Pb L_{α} , Zr L_{α} , Ti K_{α} , Nb L_{α} , Sc K_{α} , and secondary electrons were recorded photographically. Possibilities of inhomogeneous distribution of dopants and formations of second phases were examined by this technique. Also line scans were made as a quantitative indication of observed results.

X-ray diffraction was done on both powder specimens and sintered pellets. The (200) rhombohedral and the (200) and (002) tetragonal peaks were scanned at $1/8^{\circ}$ per minute to determine the proportions of the low temperature phases present. Also, slow scans were used to search for second phases. Moon's X-ray powder data of the lead zirconate-titanate system was used to index the data.¹⁵

Ferroelectric hysteresis loops were measured with a 60 cycle Sawyer-Tower circuit with 60, 110, 210 volts per mil. Sintering specimens were fabricated into 3/4 in. x 60 mil. samples and 3/8 in. diameter electrodes were applied. Data was recorded by means of an oscilloscope camera. Specimens of 1 at.% Nb, 1 at.% Sc, and pure material from previous experiments were used for additional data.

Density versus time curves were determined for various times at 1200°C and 1150°C for the 1.5 at.% niobium doped material and at 1300°C for the 1.5 at.% scandium-1.5 at.% niobium and the 3.0 at.% scandium-1.5 at.% niobium doped material. The X-ray value of 8.00 gr/cm³ for theoretical density of the 53-47 composition was used to calculate relative density.

A mercury immersion apparatus was used with an Ainsworth balance to obtain density measurements to an accuracy of approximately ±1/2 percent. Grain size measurements were made with a Jeolco scanning electron microscope. The intercept technique of multiplying 1.5 times the number of grains intercepted by randomly drawn lines across a photomicrograph was used. Polish and etch techniques were utilized where densities permitted. Otherwise, fired surfaces were measured.

Sintering times that exceeded 2000 minutes required that the packing powder be changed every 2000 minutes to prevent any weight loss due to lead oxide evaporation from the crucible.

III. RESULTS AND DISCUSSION

Sintering

A graph of the relative density versus (time)^{1/2} is given in Fig. 2 for the three different compositions at 1150°C, 1200°C, and 1300°C. The suppression of sintering by the addition of scandium to the niobium doped material is evident. Table IV and Fig. 2 show an order of magnitude change in the rate of sintering with small compositional variation. It is thought that the enhancement and suppression of lead vacancies by niobium and scandium respectively through a charge balance mechanism is responsible for the observed behavior.

Table IV. Sintering

<u>300 minutes - 1200°C</u>	<u>Percent of theoretical density</u>
1.5 at.% Nb	96%
1.5 at.% Nb 1.5 at.% Sc	66%
1.5 at.% Nb 3.0 at.% Sc	67%
 <u>300 minutes - 1300°C</u>	
1.5 at.% Nb	-
1.5 at.% Nb 1.5 at.% Sc	73%
1.5 at.% Nb 3.0 at.% Sc	72%

All green densities 63%.

The end point density for the 1.5 at.% Nb doped material is partially due to pores in the interior of grains. The niobium did not suppress

grain growth enough to allow the pores to remain on the grain boundaries. Pores in the interior of grains were experimentally observed with the scanning electron microscope on a polished section.

A larger portion of the porosity observed in the 1.5 at.% Nb specimens that had been sintered to their end point density was located on the grain boundaries of specimens. Somewhat larger grains were associated with these pores indicating that the predominating mechanism causing the end point density is a secondary grain growth. Entrapment of gas in closed pores is not suspected because Atkin sintered 2.0 at.% Nb doped material to higher densities and smaller grain size at 1200°C.² It may be concluded that 1.5 at.% Nb is an insufficient amount to suppress grain growth to the extent required to obtain theoretical density in lead zirconate titanate.

The relative density versus (time)^{1/2} plot at 1300°C and for times up to 8000 minutes is shown in Fig. 3 for the 1.5 at.% Nb-1.5 at.% Sc and 1.5 at.% Nb-3.0 at.% Sc compositions. A scandium-zirconium equilibrium second phase was observed by X-ray diffraction and microprobe techniques in the 1.5 at.% Nb-3.0 at.% Sc samples. The presence of this second phase may be responsible for the kink in the sintering curve shown in Fig. 3 for this composition.

Grain Growth

The grain size versus log time is given in Fig. 4 for the different compositions. The grain size measurements indicated regular grain growth at 1150°C and 1200°C for the 1.5 at.% Nb composition even though the microstructure of the specimen that reached an end point density shows evidence of secondary grain growth. Kingery shows that the rate of grain

growth is inversely proportional to grain size.⁶ This relationship may be expressed in the form of:

$$D^2 - D_0^2 = K(t - t_0)$$

K = proportionality constant

D_0 = grain size upon initiation of grain growth

D = grain size at time t

t_0 = time at temperature that grain growth is initiated

whereby $D^2 - D_0^2$ versus time may be plotted to obtain a straight line. This plot is given in Fig. 5 for the 1.5 at.% Nb composition at 1150°C and 1200°C. The reason for the lack of grain growth in the scandium doped samples is probably due to the fact that the porosity never reached a low enough value during sintering to allow grain boundary movement.

Weight Change

The weight loss data indicated that the postulated reaction in the 1.5 at.% Nb-3.0 at.% Sc specimens for the formation of oxygen vacancies was not occurring. The 1.5 at.% Nb-3.0 at.% Sc specimens were losing on the average 3.0 wt.% lead oxide while the other compositions lost less than .2 wt.% lead oxide during sintering; the latter were within experimental error. The compositions were titrated with lead nitrate and scandium nitrate so that no weight change should have occurred if the postulated reactions were correct.

The formation of a scandia zirconia second phase in the 1.5 at.% Nb-3.0 at.% Sc specimen may be responsible for the observed weight loss. It is proposed that excess scandia reacted with zirconium ions in the

lead zirconate titanate, and the products of this reaction were a scandia-zirconia phase and lead oxide vapor. This lead oxide vapor left the sample, giving the observed weight change.

X-ray

The X-ray diffraction results indicated that both the rhombohedral and tetragonal phases of lead zirconate titanate were present in all three compositions. The presence of both phases may be expected since the 53-47 composition is located near the low temperature phase boundary. The niobium material tended to be more tetragonal while the niobium-scandium material had a higher proportion of the rhombohedral phase. A further indication of the existence of an equilibrium scandium-zirconium second phase in the 1.5 at.% Nb-3.0 at.% Sc material was given by comparing the X-ray patterns of the two scandium-niobium doped materials. The 1.5 at.% Nb-3.0 at.% Sc material had a larger proportion of tetragonal phase than the 1.5 at.% Nb-1.5 at.% Sc material because the excess scandium that could not go into solution in the former reacted with the zirconia in the lead zirconate titanate. The zirconia-titania ratio in the lead zirconate titanate was then decreased, shifting the composition into the tetragonal phase region.

The 1.5 at.% Nb and 1.5 at.% Nb-1.5 at.% Sc compositions gave no indication of a second phase by X-ray diffraction. The 1.5 at.% Nb-3.0 at.% Sc specimens had discernible X-ray peaks which corresponded to cubic stabilized zirconia; the microprobe indicated this phase was of a zirconia scandia composition.

Microprobe

The microprobe results are given in Figs. 6, 7, 8. The large zirconia particles observed in the 1.5 at.% Nb-1.5 at.% Sc sample were found in all three compositions. It is thought that the 500 grams of the 12 mole batch which was ground using zirconia media was responsible for the 20 μ m chunks of zirconia occasionally found in the microstructures. The large size of the zirconia allows a non-equilibrium situation to exist even though some of the samples were held at 1300°C for 8000 minutes. The distribution of these particles was widely scattered in the microstructure and it is thought that they had little effect on the overall observed behavior of this material.

The 1.5 at.% Nb-3.0 at.% Sc sample indicated an equilibrium second phase of a scandium zirconium compound as shown in Fig. 8. The microprobe showed that the phase was homogeneously distributed throughout the specimen in micron sized inclusions. The 3.0 at.% addition of scandium exceeded the solubility limit in the 1.5 at.% Nb doped lead zirconate titanate system and the excess scandium exhibited a strong affinity for zirconium.

The observation of an equilibrium scandium zirconium phase in this specimen is reinforced by the weight loss behavior, the X-ray diffraction results and the hysteresis loop data.

A line scan was made with the microprobe to quantitatively determine if the scandium concentration in the 1.5 at.% Nb-1.5 at.% Sc and the 1.5 at.% Nb-3.0 at.% Sc specimens was the same in the lead zirconate titanate matrix. The beam travelled 100 μ m across the specimens in 1 μ m steps while recording the number of counts per ten seconds. The position

of the beam could be monitored by an optical microscope; thus when the beam intersected a pore or a second phase in the 1.5 at.% Nb-3.0 at.% Sc specimen, the count could be excluded. The results of this technique gave an average count of 874 with a standard deviation of 8.2% for the 1.5 at.% Nb-1.5 at.% Sc specimen while the 1.5 at.% Nb-3.0 at.% Sc specimen yielded an average count of 1030 and a standard deviation of 11.2% for Sc K_{α} radiation. A difference between the averages of approximately two standard deviations indicates a slightly higher concentration of scandium in the lead zirconate titanate phase in the 1.5 at.% Nb-3.0 at.% Sc specimens. This indicated that the solubility limit of scandium in 1.5 at.% Nb doped lead zirconate titanate is slightly above 1.5 at.%.

The lead zirconate titanate lattice apparently has little tendency to accommodate scandium ions by the formation of anion vacancies. The only mechanism for incorporating measurable amounts of scandium into the lattice is to add an equivalent number of plus five ions to preserve electrical neutrality.

Ferroelectric Hysteresis Loops

The ferroelectric hysteresis loops of the different doping levels of niobium and scandium are given in Figs. 9 and 10. There are several trends shown in the ferroelectric parameters with changing composition. Increasing the niobium content caused P_s and P_r to increase while the coercive field remains constant in the 1.0 and 1.5 at.% Nb doped specimens. The reduction of P_s by an order of magnitude and complete loss of P_r with increasing scandium content is also evident in Fig. 9.

The niobium appears to counteract the effect of the scandium somewhat as shown by the comparison of the 1.0 at.% Sc doped material to

1.5 at.% Nb-1.5 at.% Sc doped material. The scandium doped material with the niobium present shows slight ferroelectric behavior relative to the 1.0 at.% Sc material.

The hysteresis loops shown in Fig. 10 with an applied field of 210 volts/mil indicates that the solubility limits of scandium for the 1.0 at.% Sc and the 1.5 at.% Nb-3.0 at.% Sc samples have been exceeded because both materials have the same ferroelectric behavior.

The trends shown by this ferroelectric hysteresis data strengthen the correlation made between domain mobility and the effect of enhancing or depressing the lead vacancy concentration by dopants. Although the second phase was present in 1.5 at.% Nb-3.0 at.% Sc doped material, it may be postulated that it should not cause the order of magnitude change in ferroelectric properties that was observed.

IV. CONCLUSIONS

The utmost importance of compositional control in ferroelectric ceramics has been experimentally shown. The reproducibility of sintering characteristics and electrical properties is dependent upon composition. The data obtained strengthens the hypothesis that lead vacancies are the controlling factors in solid state sintering and developing square loop ferroelectrics in the lead zirconate titanate system.

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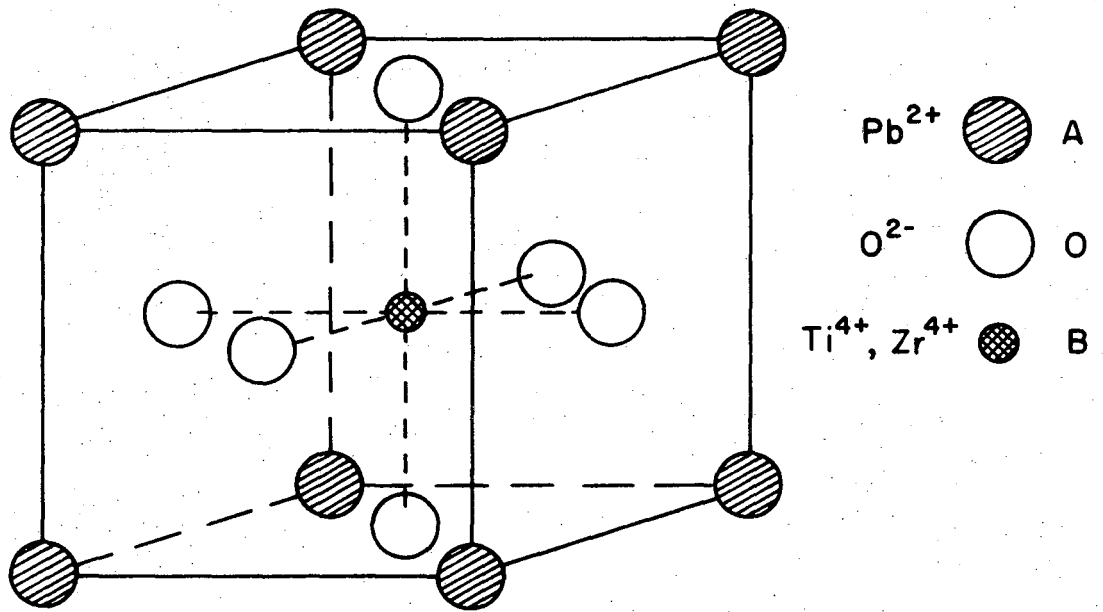
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FIGURE CAPTIONS

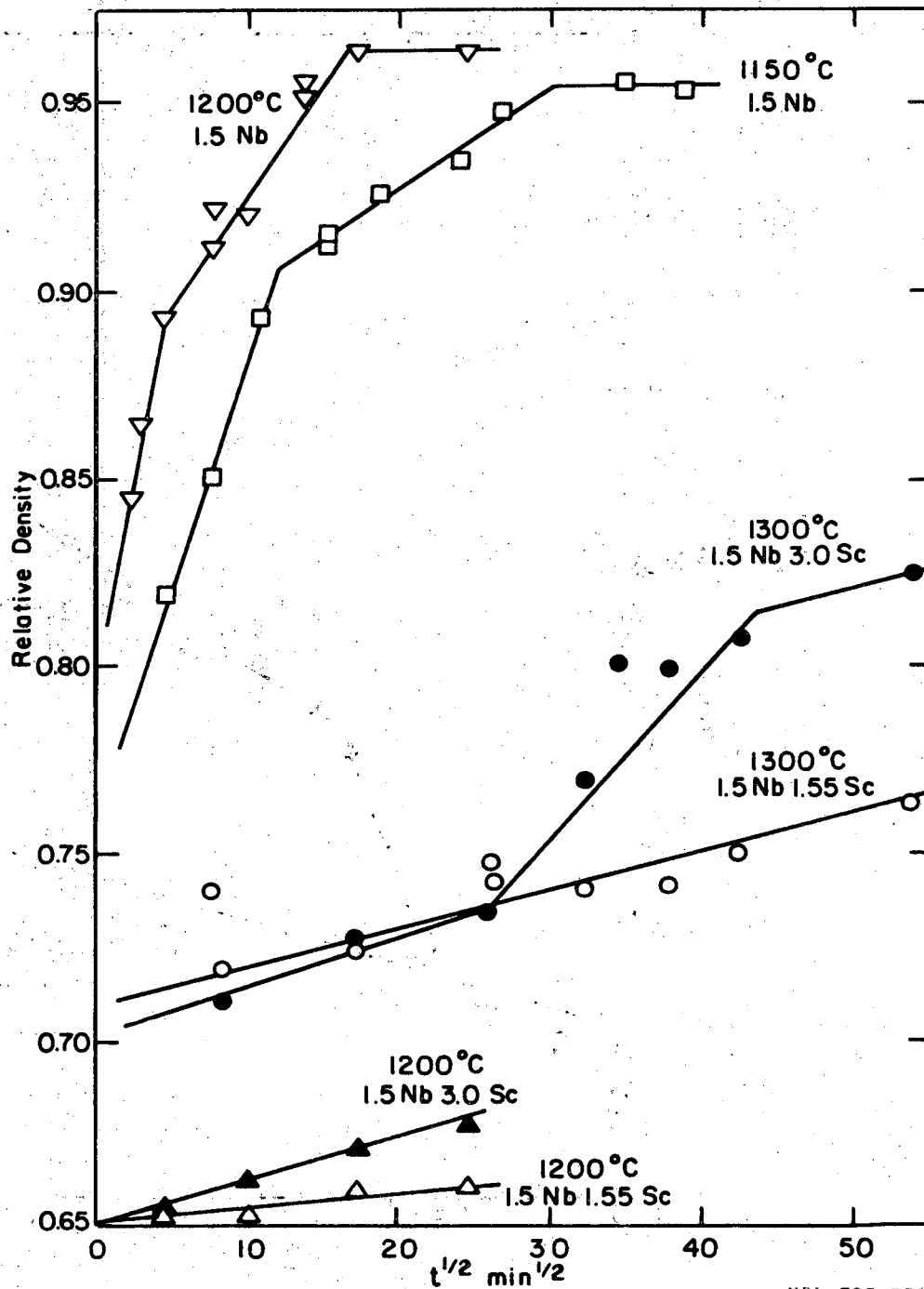
- Figure 1. Atomic structure of lead zirconate titanate
- Figure 2. Relative density vs. $(\text{time})^{1/2}$
- Figure 3. Relative density vs. $(\text{Time})^{1/2}$
- Figure 4. Grain size vs. log time
- Figure 5. $(D-D_0)^2$ vs. $(t-t_0)$
- Figure 6. Microprobe scans - 1.5 at.% Nb composition. 1000X
- Figure 7. Microprobe scans - 1.5 at.% Nb-1.5 at.% Sc composition. 1000X
- Figure 8. Microprobe scans - 1.5 at.% Nb-3.0 at.% Sc composition. 1000X
- Figure 9. Ferroelectric hysteresis loops
- Figure 10. Ferroelectric hysteresis loops



Cubic perovskite structure.⁵

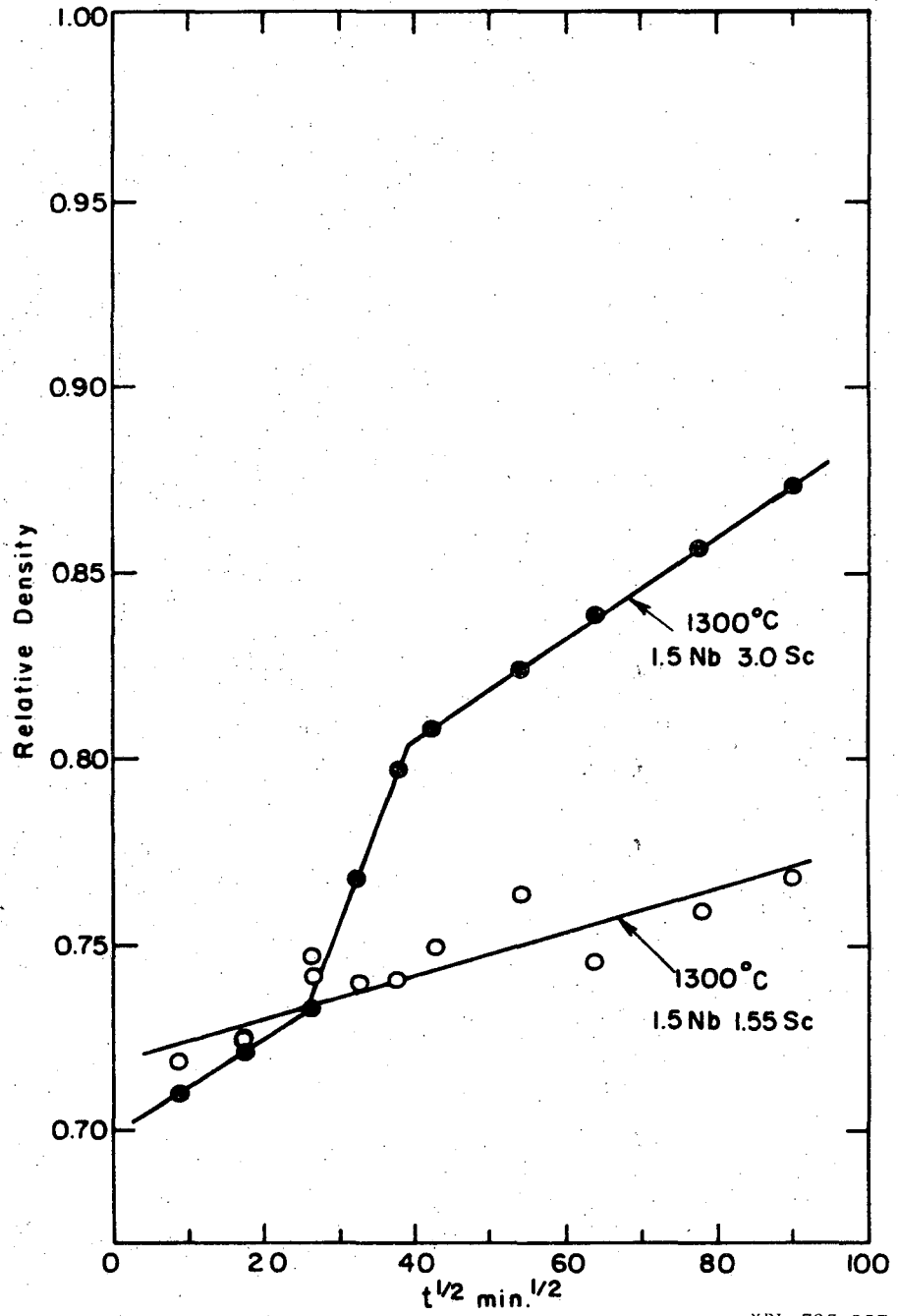
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Figure 1



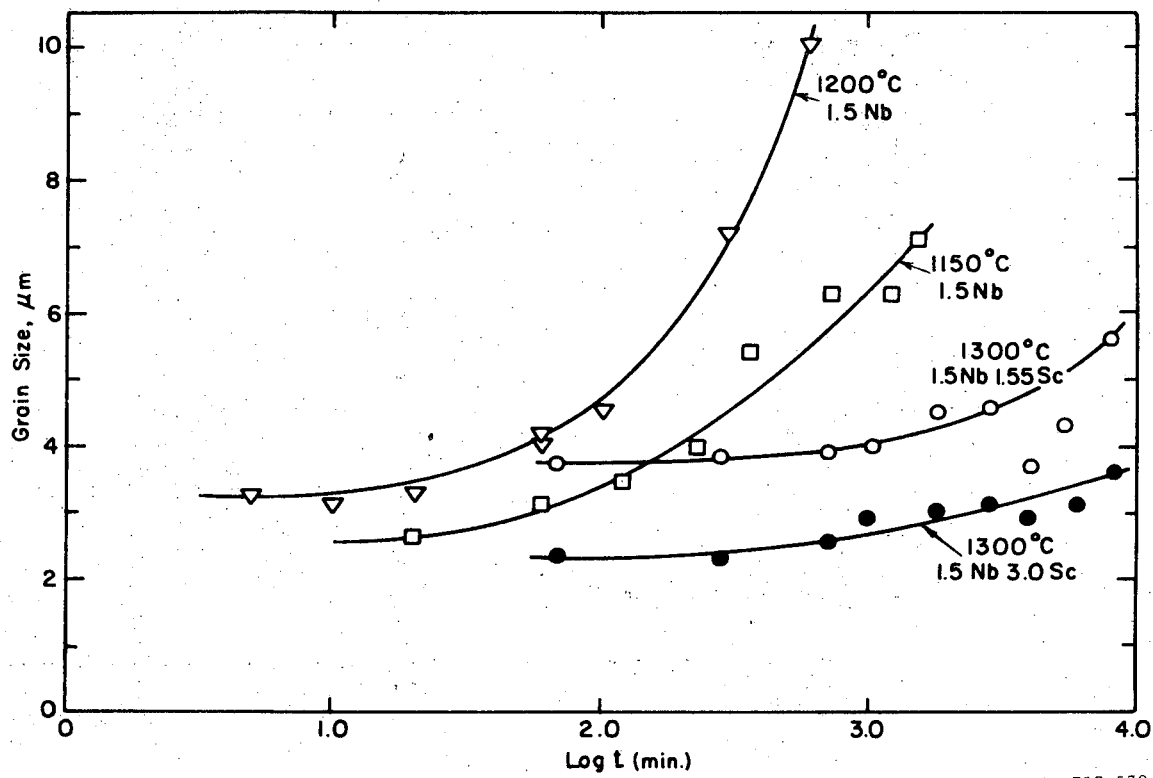
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Figure 2



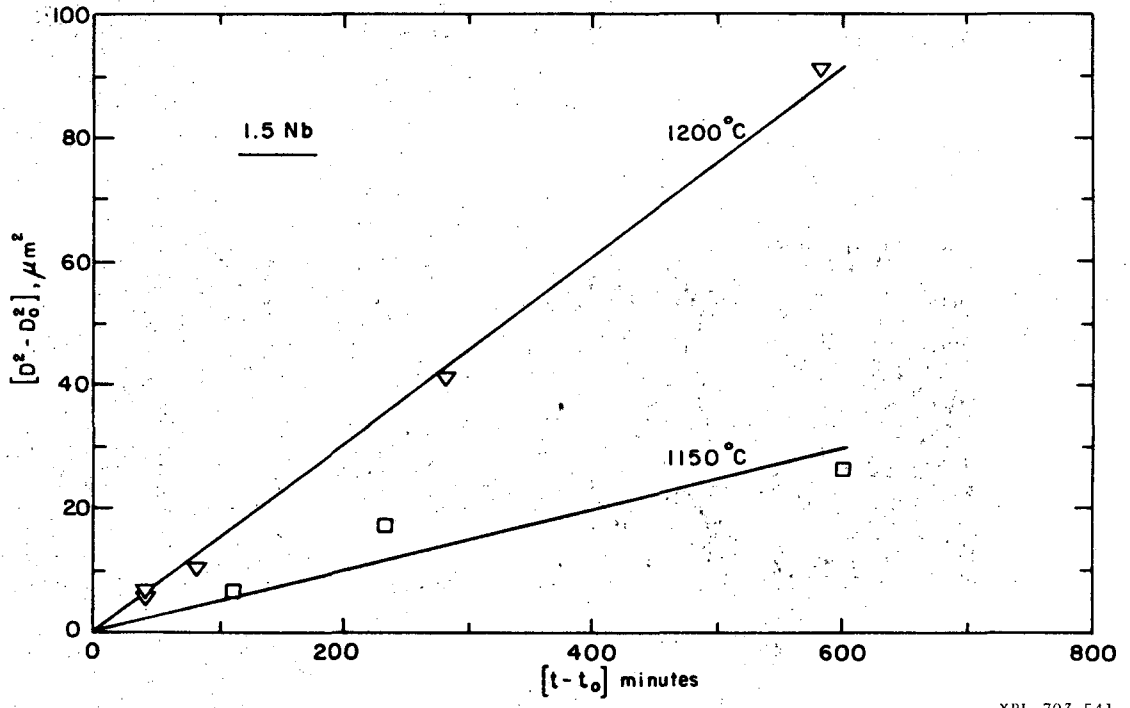
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Figure 3



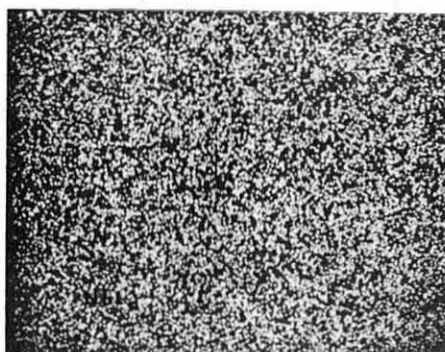
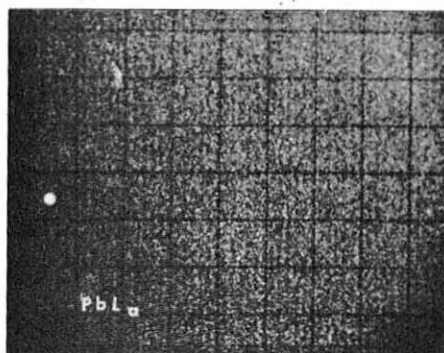
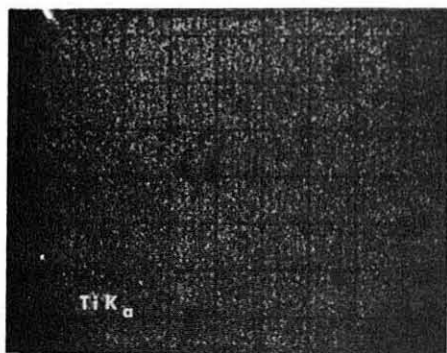
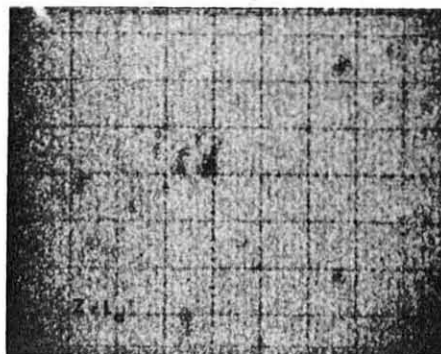
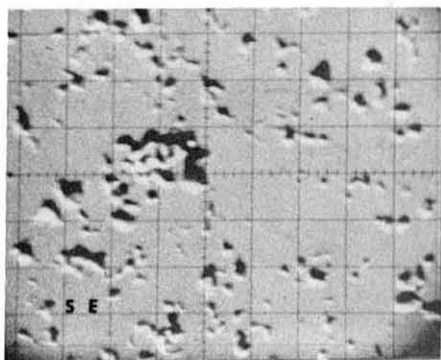
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Figure 4



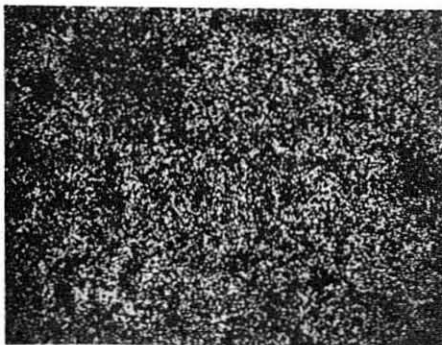
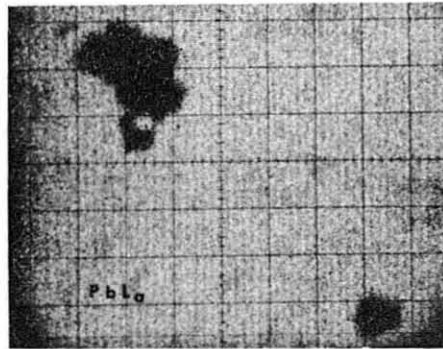
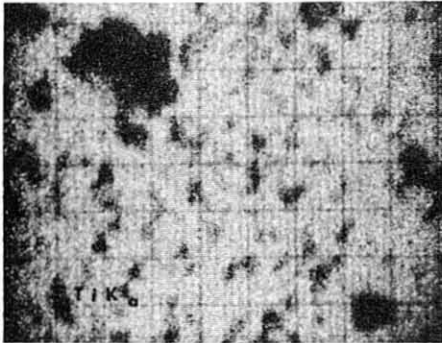
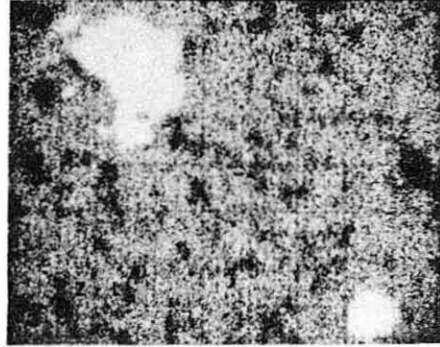
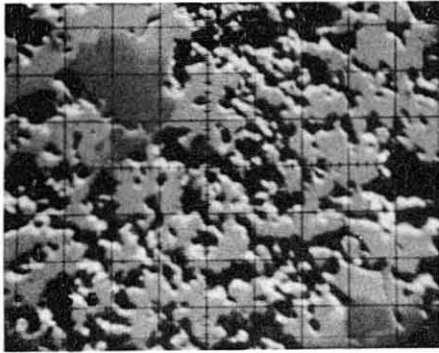
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Figure 5



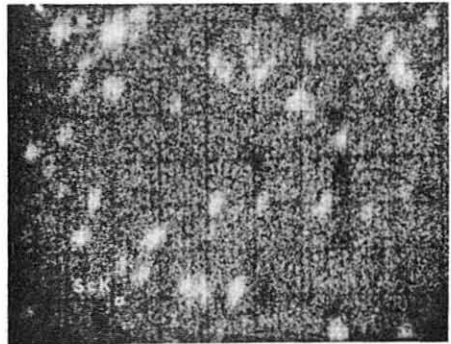
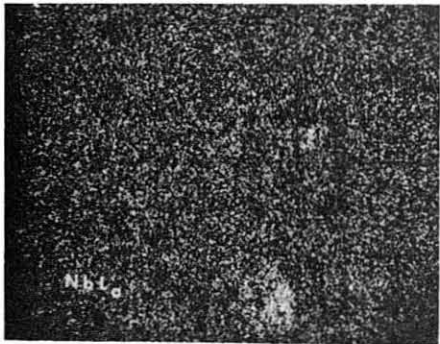
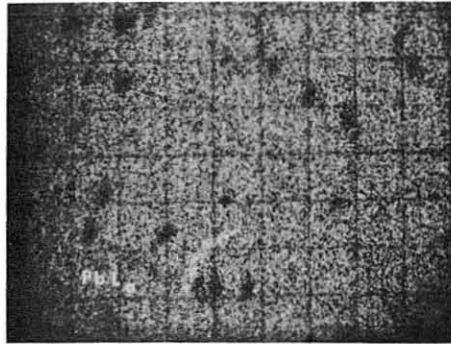
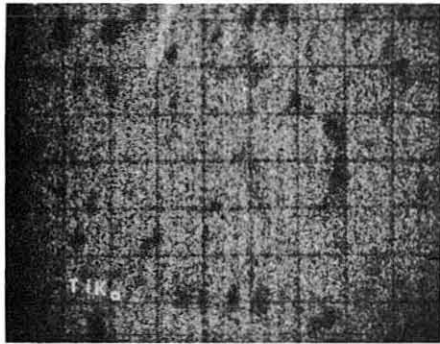
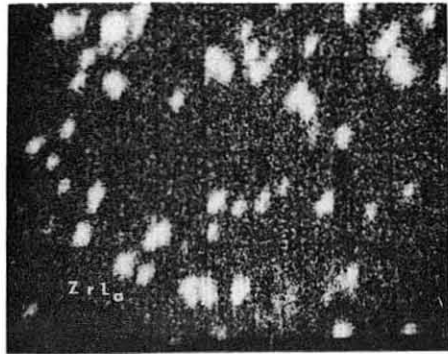
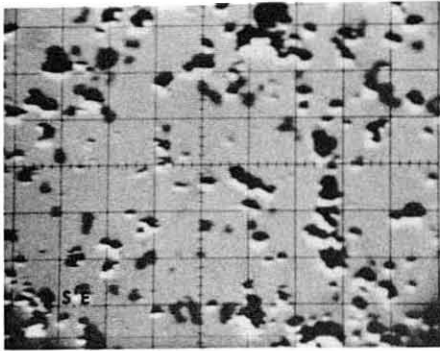
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Figure 6



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Figure 7

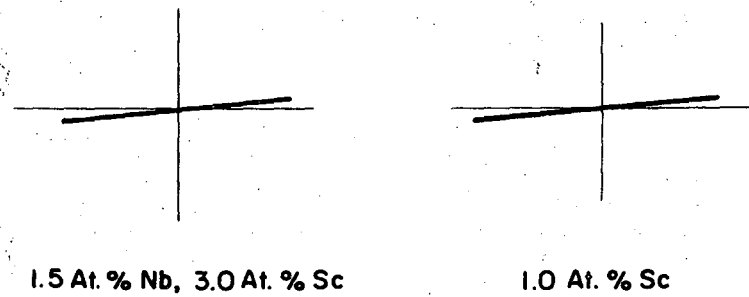
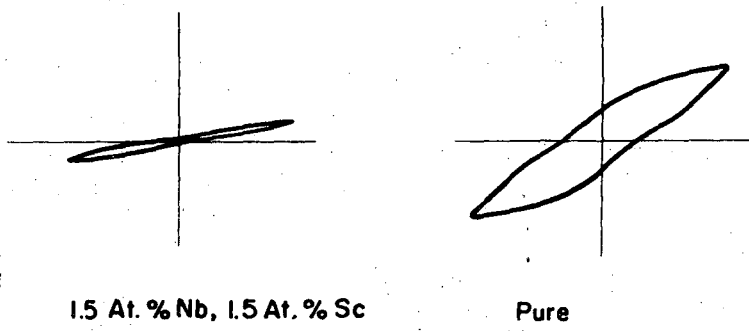
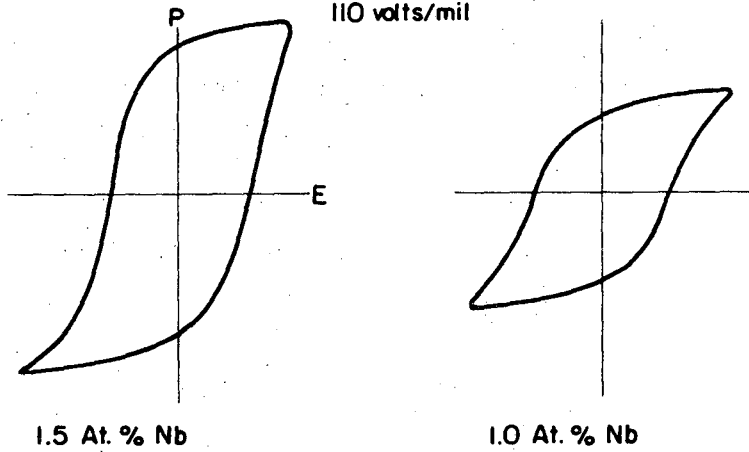


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Figure 8

Ferroelectric Hysteresis Loops

110 volts/mit

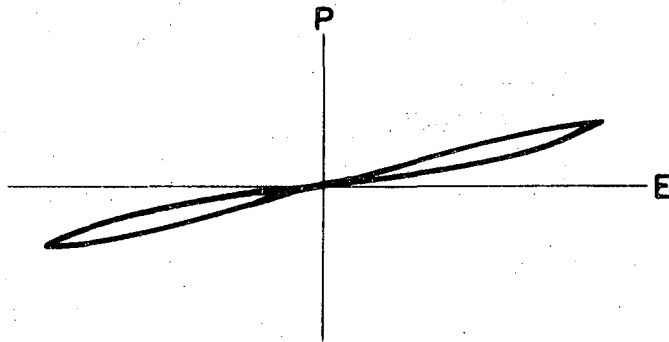


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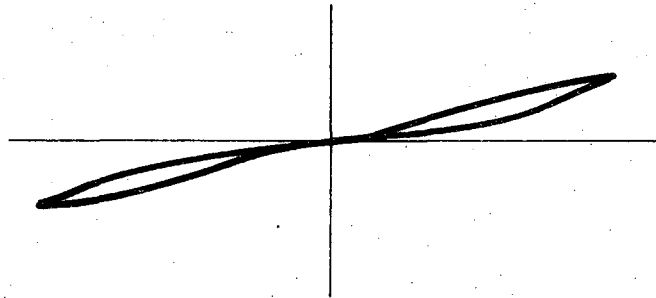
Figure 9

Ferroelectric Hysteresis Loops

210 volts/mil



1.5 At. % Nb, 3.0 At. % Sc



1.0 At. % Sc

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Figure 10

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