CONF-891020--7

SAND--89-1480C

DE90 006811

Chemically Prepared PZT Films Doped With Niobium

B.A. Tuttle, D.H. Doughty, R. Schwartz, T.J. Garino, S.L. Martinez, D. Goodnow, C.L. Hernandez and R.G. Tissot, Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185

ABSTRACT

We report on the first ferroelectric measurements of chemically prepared thin films of PZT containing niobium, (PNZT). Polycrystalline, perovskite PNZT thin films were fabricated by spin coating Pt coated SiO_2/Si substrates with alkoxide solutions. We systematically doped our base composition, PZT 53/47, with niobium (0 to 10 at%). Further compositional modifications included the variation of Zr/Ti ratio for films containing 2 at% Nb. The dielectric constants measured for PNZT 2/56/44, 2/53/47 and 2/48/52 films were in good agreement with bulk values. Dielectric constants on the order of 700, 1000 and 500, respectively, were measured for these three films. Both linear and nonlinear current-voltage behavior was observed for our Pt/PNZT/Pt device structures, depending on the amplitude of the applied voltage and the temperature of measurement. We were able to make ferroelectric films of PNZT 2/53/47 (2 at% Nb doping) with spontaneous polarizations of 0.2 C/m^2 and coercive fields of 2.5 MV/m. PNZT films containing larger niobium additions (5 and 10 at%) had inferior ferroelectric properties because of the presence of nonperovskite phases.

INTRODUCTION

PZT ($Pb(Zr_xTi_{1-x})O_3$) thin films are of considerable interest for nonvolatile semiconductor memory applications. The ideal ferroelectric film for these applications should operate at low voltages, have a large voltage difference between read and write pulses, and exhibit maximum endurance and retention. Thus, the ideal film should have the following ferroelectric properties: low coercive field, high remanent polarization, minimal aging and

---

minimal fatigue. Examples of other factors that may influence the compositional choice of ferroelectric films for nonvolatile semiconductor memory devices are piezoelectric effects and the dielectric constant.

Our initial efforts have emphasized the fabrication and characterization of niobium doped PZT thin films near the morphotropic phase boundary (PZT 53/47). Bulk PZT ceramics that are compositionally near the morphotropic phase boundary have large remanent polarizations (0.4 to 0.5 C/m^2) and reasonable coercive fields (2 to 3 MV/m). Donor doped bulk PZT ceramics have lower coercive fields and higher resistivities than undoped PZT ceramics. Further, dielectric aging rates[1] in donor doped PZT ceramics are much lower than for undoped ceramics. Until now, no one has fabricated PZT thin (< 5 μm) films with niobium additions. For these reasons, we have investigated donor doping (Nb) in chemically-prepared PZT thin films near the morphotropic phase boundary.

A review of donor doping in bulk PZT ceramics is appropriate, since both resistivity and ferroelectric properties are substantially affected by dopants. Undoped PZT ceramics exhibit p-type conduction and have a resistivity on the order of 10^{10} ohm-cm. The p-type conduction in these materials is explained[1] by the creation of holes due to an intrinsic excess of lead vacancies compared to oxygen vacancies. Holes are formed in the vicinity of these Pb vacancies as shown in equation 1.

$$V_{Pb} \text{ -----> } V_{Pb}^{''} + 2h^{\bullet\bullet} \qquad (1)$$

Niobium doping increases the resistivity of bulk PZT. For 1 at% Nb doping, there is complete compensation[1] of intrinsic holes by the donor electrons. The resistivity of PZT ceramics containing 1 at% Nb is approximately 10^{13} ohm-cm. As the niobium doping level is increased above 1 at%, the resistivity remains constant and the coercive field decreases. Both these phenomena are explained by the creation of Pb vacancies[1] to maintain electroneutrality (equation 2).

$$Nb_2O_5 \xrightarrow{PZT} 2\,Nb_{Zr}^{\bullet} + V_{Pb}^{''} + PbO\uparrow + 2O_2\uparrow \qquad (2)$$

The solid solubility limit for Nb in bulk PZT ceramics is approximately 3 at% Nb. As Nb doping is increased above this limit, Nb_2O_5 is formed and PNZT ceramics with inferior electrical properties result.

PbO volatility in bulk PZT ceramics fired above 1000°C facilitates the formation of lead vacancies and the accomodation of the aliovalent Nb ion into solid solution. It has not been demonstrated that chemically prepared PNZT films processed at 650°C, where PbO volatility is nonexistent or greatly reduced, will form lead vacancies. Thus, it is not certain that chemically prepared PZT films with Nb additions, processed at temperatures of 650°C, will exhibit higher resistivities and lower coercive fields than undoped PZT films. Therefore, a major goal of our study is to determine if chemically prepared niobium doped PZT films have larger resistivities and lower coercive fields than undoped films.

Solution chemistry techniques have been used to enhance densification at low temperatures for a variety of inorganic materials. PZT and PLZT thin films, which have good ferroelectric properties, have been fabricated[2-5] using process temperatures 600°C below the sintering temperature for bulk PZT. Lipeles et al[5] developed a process, using isopropanol solutions of lead 2-ethylhexanoate, zirconium tetra-n-propoxide and titanium tetra-n-butoxide for the formation of single phase perovskite PZT 55/45 films. Extensive hydrolysis of the alkoxides in the starting solution resulted in amorphous films that contained considerable porosity. Lower water additions (mole ratios of water to metal ions equal to 0 or 0.5) were essential for the fabrication of perovskite PZT films at 525°C. We have used the Lipeles process, with slight modifications, for the fabrication of niobium doped PZT films.

EXPERIMENTAL PROCEDURE

Alkoxide derived solutions (0.25 M) were prepared from precursors of lead 2-ethylhexanoate, zirconium tetra-n-butoxide, titanium tetraisopropoxide and niobium pentaethoxide for the fabrication of PNZT films. Immediately before deposition, these solutions were filtered with a 0.2 μm syringe filter. The filtered solutions were then deposited onto our substrates at 4000 RPM using a photoresist spinner. The film was dried at 150°C for 20 minutes and then given a 400°C/20 minute heat treatment to decompose residual organics. If desired, additional film coatings could be deposited after the 400°C heat treatment. Typically, our films consisted of 3 layers and were 410 nm thick after firing. Scanning electron micrographs and NIST micron standards were used to determine film thickness. A final

annealing treatment at temperatures ranging from 600°C to 725°C was used to crystallize perovskite PNZT films. For the final anneal, heating rates of 3°C/min, cooling rates of 1.5°C/min, and soak times of 30 minutes or 1 hour were used.

Our substrates consisted of 4" diameter (100) silicon wafers onto which a 600 nm thick, tetraehylorhosilicate (TEOS) derived SiO_2 layer was vapor deposited and densified at 950°C. We dc sputter deposited a 200 nm layer of Pt on top of the SiO_2. This Pt layer served as the bottom electrode for the PNZT film. For some of our PNZT films, a 50nm Ti adhesion layer was sputter deposited under the bottom Pt film layer. The top electrode for our PNZT films consisted of a sputter deposited array of Pt dots. These dots were of three different diameters: 0.5 mm, 0.75 mm or 1.0 mm. Deposition conditions for the top electrodes were similar to those for the bottom electrode. Typically, the Pt films were 200 nm thick and deposited at a rate of 10 nm/minute.

Electrical contact to the bottom electrode was achieved by careful mechanical abrasion of the fired PNZT film to expose a selected area of the electrode. Silver epoxy was then used to facilitate connection of the bottom electrode to our microprobe. Relatively blunt microprobes ($\approx$ 100 μm diameter) were used for our electrical measurements, to minimize film damage. Our resistance measurements were performed using a two point probe technique. A sensitive ammeter (Keithley Model 619 electrometer) was required to measure the low currents (less than 1 nA) for our electrical tests.

Our device structure was chosen to be representative of ferroelectric film configurations in nonvolatile semiconductor memory devices. This device structure, consisting of a thin insulating film between two conductive layers, made meaningful 4 point probe measurements impossible. We performed resistance measurements at a variety of voltage levels to ascertain the nonlinear behavior of our films. Typically, each measurement was made 5 to 20 minutes after the initial voltage application to allow stabilization of both the electrometer and ferroelectric domain motions within the film. Resistance measurements were made as a function of temperature by placing the films on a hot chuck, with temperature control to 300°C. In addition to the thermocouple inside the chuck, an external copper-constantan thermocouple (0.125 mm diameter wire) was attached to the top of the film for temperature monitoring. Although a modified Diamant-Pepinsky bridge was used for the ferroelectric measurements, all ferroelectric measurements presented in this paper were uncompensated.

RESULTS AND DISCUSSION

Figure 1 depicts thermogravimetric and differential thermal analyses for gel particles of PNZT 2/53/47. These gel particles were formed by drying a PNZT gel at 150°C for approximately 1 hour and then crushing the dried gel into particles of less than 500 μm diameter. We interpret the sequence of DTA exotherms, with increasing temperature, to correspond to organic decomposition, pyrochlore crystallization and perovskite formation, respectively. Consistent with the gels, high temperature X-ray diffraction traces of our PNZT 2/53/47 films indicate that the formation of the pyrochlore phase occurs at a lower temperature than the perovskite. However, the initial crystallization of perovskite PZT may be from remanent amorphous phases rather than the pyrochlore. PZT 53/47 gel particles with other niobium additions (0 to 10 at%) had DTA and TGA traces similar to those in Figure 1. The crystallization temperature (less than 500°C) of perovskite PZT 53/47 is slightly lower for our gels than that reported (approximately 550°C) for an alternative chemical synthesis technique.[2]

Figure 2 depicts X-ray diffraction traces of three films of the PZT 50/50 composition. These 3 films were 410 nm thick and were fired for 30 minutes at 3 different temperatures: 570°C, 610°C, and 645°C. From thermal analyses of gel particles (Figure 1) single phase perovskite PZT is expected for a thermal treatment of 570°C for 30 minutes. Although significant perovskite PZT is present, there is extensive formation of a low temperature pyrochlore phase in the the film fired at this temperature. The diffraction trace of the film fired at 570°C contains every diffraction peak ($10° < 2\theta < 60°$) of the $Pb_2Ti_2O_6$ oxygen deficient pyrochlore.[6] Interestingly, there is little evidence in the diffraction trace of this 570°C film for the existence of the PbO deficient $PbTi_3O_7$ pyrochlore.[7] Thus, PbO volatility does not appear to influence phase evolution for these thermal processing conditions. The PZT 50/50 film fired at 645°C was single phase perovskite by X-ray diffraction analysis. Our PNZT 2/53/47 films, fired at 650°C for 30 minutes, produced similar single phase perovskite X-ray diffraction patterns.

Initial measurements indicated our PNZT 2/53/47 films had a resistivity of 10^{12} ohm-cm for an applied field of 2.5 MV/m. However, current measured as a function of applied voltage at 25°C was represented by the following nonlinear relationship.

$$I(X\ 10^{10}A) = 0.84\ V^2 + 0.12\ V + .06 \qquad (3)$$

This strong second order voltage dependence was observed from 1.25 to 12.5 MV/m for our films. The implication is that a potential barrier at the Pt/PZT interface, rather than the PNZT film resistivity, dominated our measurement at 25°C. Current-voltage characteristics, measured at 100°C, for the PNZT 2/53/47 film were linear from 0 to 5.0 MV/m dc. Above 5.0 MV/m, a slight nonlinear (less than second order) dependence was observed. Current-voltage measurements at 300°C indicated the film response was linear over a much narrower range of applied field (0 to 0.5 MV/m). Further, the nonlinear behavior at higher fields, measured at 300°C, was much greater than second order.

Although we do not have definitive proof of the cause of the current-voltage behavior with temperature, we offer the following hypothesis. We feel that a potential barrier at the PZT film - Pt electrode interface influences the resistivity measurements at 25°C. As temperature is increased to 100°C, a linear I-V characteristic, which perhaps represents the true resistivity of the PNZT film, is measured. We feel the extremely nonlinear behavior at high temperatures (>150°C) and high fields is due to the nonlinear nature of PZT under these high electrical and thermal stress conditions. We have performed a calculation that indicates that the current measured at 100°C and above should not be influenced by the potential barrier. For this calculation, we assume the magnitude of the current measured at room temperature is solely due to a potential barrier greater than 2 eV. We then use the resistivity values and activation energy for bulk PZT to show that the current measured above 100°C is representative of the PZT film rather than the potential barrier at the interface. It must be emphasized that further data is required to support our hypothesis. Electron affinities and surface state densities are among the parameters that need to be known to adequately prove or disprove the model.

Figure 3 is a plot of log resistivity vs 1000/T(K) comparing our PNZT 2/53/47 film fired at 650°C/30 min with doped and undoped bulk PZT[1] ceramics. The 2 to 3 order of magnitude difference in resistivity for doped bulk PZT compared to undoped bulk PZT is readily apparent. Our film has resistivity values that are intermediate to the bulk PZT materials. Our film was ferroelectric, having a spontaneous polarization of 0.22 C/m^2, and had low field (0.25 MV/m) dielectric constants in excess of 1000. The activation energy for the bulk PZT conductivity is on the order of 0.9 eV. Disturbingly, the activation energy for our PNZT film was approximately 0.55 eV. Film conduction may be

influenced by factors such as stress in the film, space charge effects and the presence of a minor amount of pyrochlore (undetectable by X-ray diffraction analysis). Any of these factors may lower the activation energy. In addition, convection from the surface of our films may cause the true film temperature to be different than that recorded by the thermocouple.

Ferroelectric properties of PZT 53/47 films were substantially affected by niobium doping. Figure 4 compares a well saturated hysteresis loop of a PZT 53/47 film with 2 at% Nb addition with a low polarization, high coercive field hysteresis loop of an identically processed film with 10 at% Nb addition. There was little change in the polarization values of identically processed films with 2 at% and 0 at% Nb additions. A reasonable decrease in the coercive field, from 4.0 MV/m to 2.5 MV/m, was observed for the film with 2 at% Nb compared to the film that was not doped. Films with 5 and 10 at% Nb were not single phase perovskite. This was not due to the exsolution of Nb_2O_5, but because a substantial amount of pyrochlore was present in these films. Attempts were made to fire these films at higher temperatures to produce single phase perovskite films. Although the percentage of perovskite phase increased with firing temperature, firing temperatures in excess of 775°C resulted in the formation of other nonperovskite phases. As expected, films doped with 5 and 10 at% Nb had lower polarizations, lower dielectric constants and higher coercive fields than films doped with 2 at% Nb or less.

A brief investigation of PNZT films with different Zr/Ti ratios was made. We fabricated films of three different Zr/Ti ratios: 1) PNZT 2/48/52, 2) PNZT 2/53/47, and 3) PNZT 2/56/44. All three films were 410 nm thick, fired at 650°C for 30 min and exhibited ferroelectric hysteresis loops. Figure 5 contains a plot of the dielectric constant of our PNZT films as a function of Zr/Ti ratio. We have also plotted data presented by Sayre et al.[8] in their paper on RF sputtered PZT films. Figure 5 indicates our process gives good control of the Zr/Ti ratio, 1 mol% or better, since the dielectric constant peaks at the morphotropic phase boundary, as it does for bulk ceramics. The magnitude of the dielectric constant for our unpoled films agrees very well with both bulk ceramics and Sayre's 3 micron thick films. For our dielectric measurements, we used an ac field of 0.25 MV/m amplitude (0.1 volt) and measured dissipation factors in the range of 0.03 to 0.06.

Our PNZT film polarization values, measured from ferroelectric hysteresis loops, were less than the polarizations of Sayre's 3μm sputtered PZT films. However, the ferroelectric polarizations, measured for our 0.4 μm thick films, were slightly greater than those of his 1 μm thick sputtered films. Our PNZT 2/53/47 film had significantly larger polarizations than either of our two films which were compositionally removed from the morphotropic phase boundary (PNZT 2/56/44 or PNZT 2/48/52). This polarization behavior as a function of Zr/Ti ratio was also observed for Sayre's sputtered films[8] and bulk PZT ceramics.[1]

Summary:

We have fabricated and characterized chemically prepared PZT films doped with niobium. Although resistivity measurements of PNZT 2/53/47 films at room temperature indicated nonlinear behavior, linear I-V behavior was observed over reasonable ranges of applied field at elevated temperatures. If PNZT film resistivity is responsible for this linear behavior, PNZT 2/53/47 film resistivities of 10^{11} ohm-cm were measured at 100°C. Although this resistivity is greater than that of undoped bulk PZT ceramics, we cannot yet conclude that donor doping is responsible for the increased resistivity in these films processed at 650°C. Further studies are required to eliminate the effects of film process variations and to develop a technique to measure the true PNZT film resistivity. Films with large niobium additions had lower dielectric constants, lower polarizations, and higher coercive fields than films doped with 2 at% Nb or less. We attribute this behavior to the significant amount of nonperovskite phase in films with large niobium additions.

REFERENCES

1. B. Jaffe, W. Cook, and H. Jaffe, Piezoelectric Ceramics, Academic Press, (1971).

2. K. Budd, S. Dey, and D. Payne, "Sol-Gel Processing of $PbTiO_3$, $PbZrO_3$, PZT and PLZT Thin Films," Brit. Ceram. Soc. Proceedings, 36, 107-20 (1985).

3. A. Shikh and G. Vest, "Kinetics of $BaTiO_3$ and $PbTiO_3$ Formation From Metallo-Organic Precursors," J. Am. Ceram. Soc. 69, [9] 682-88 (1986).

4. J. Xu and R. Vest, "Preparation and Properties of PLZT Films From Metallorganic Precursors," Am. Ceram. Soc. Bull., 67 [3] 598 (1988).

5. R. Lipeles, D. Coleman, M. Leung, "Effects of Hydrolysis on Metallo-Organic Solution Decomposition of PZT Films," MRS Symposium Proceedings, 73, 665-70 (1986).

6. F. Martin, "A Metastable Cubic Form of Lead Titanate Observed in Titania Nucleated Glass Ceramics," Phys. Chem. of Glasses, 6 [4] 143-7 (1965).

7. K. Iijima, Y. Tomita, R. Takayama, and I. Ueda, "Preparation of c-axis Oriented $PbTiO_3$ Thin Films and Their Crystallographic, Dielectric and Pyroelectric Properties," J. Appl. Phys., 60 [1] 361-7 (1986).

8. K. Sreenivas, M. Sayer, and P. Garrett, "Properties of DC Magnetron Sputtered Lead Zirconate Titanate Thin Films," Thin Solid Films, 172 [2] 251-67 (1989).

Figures

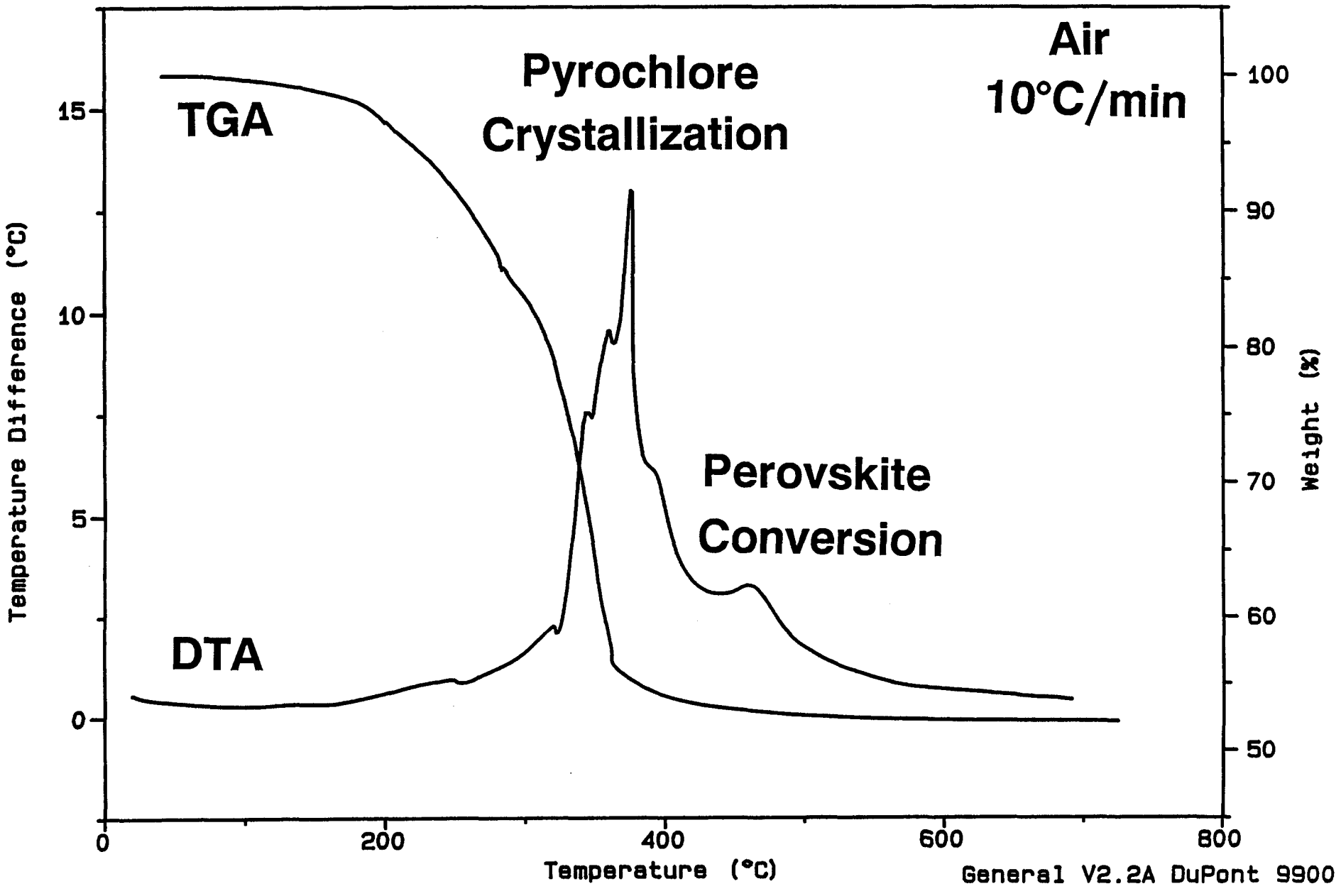
Figure 1. Thermal analyses of PNZT 2/53/47 gel particles show formation of perovskite phase below 500°C.

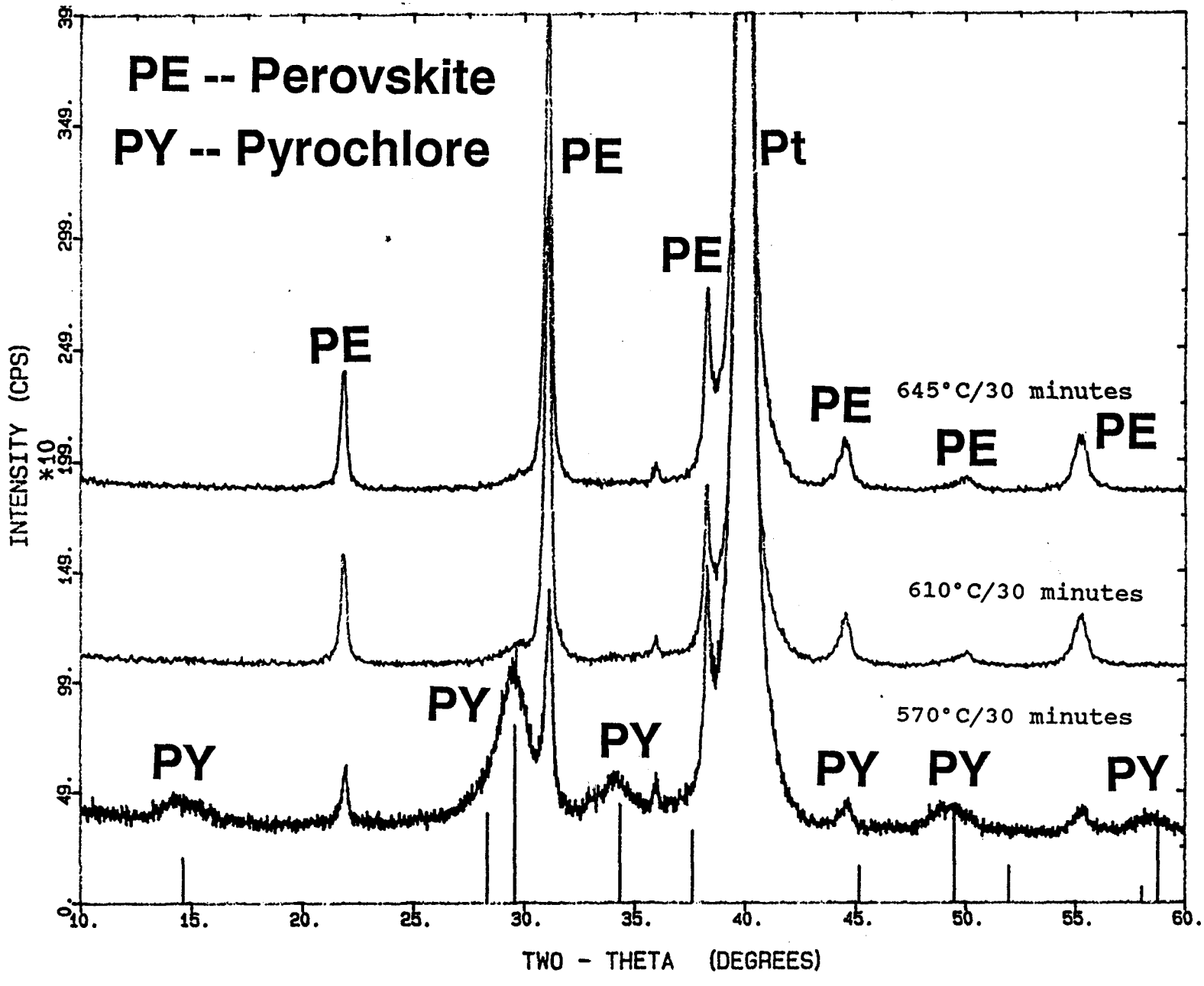
Figure 2. X-ray diffraction patterns of PZT 50/50 fired at three different temperatures: 570°C, 610°C, and 645°C, indicates elimination of pyrochlore phase with increased firing temperature.

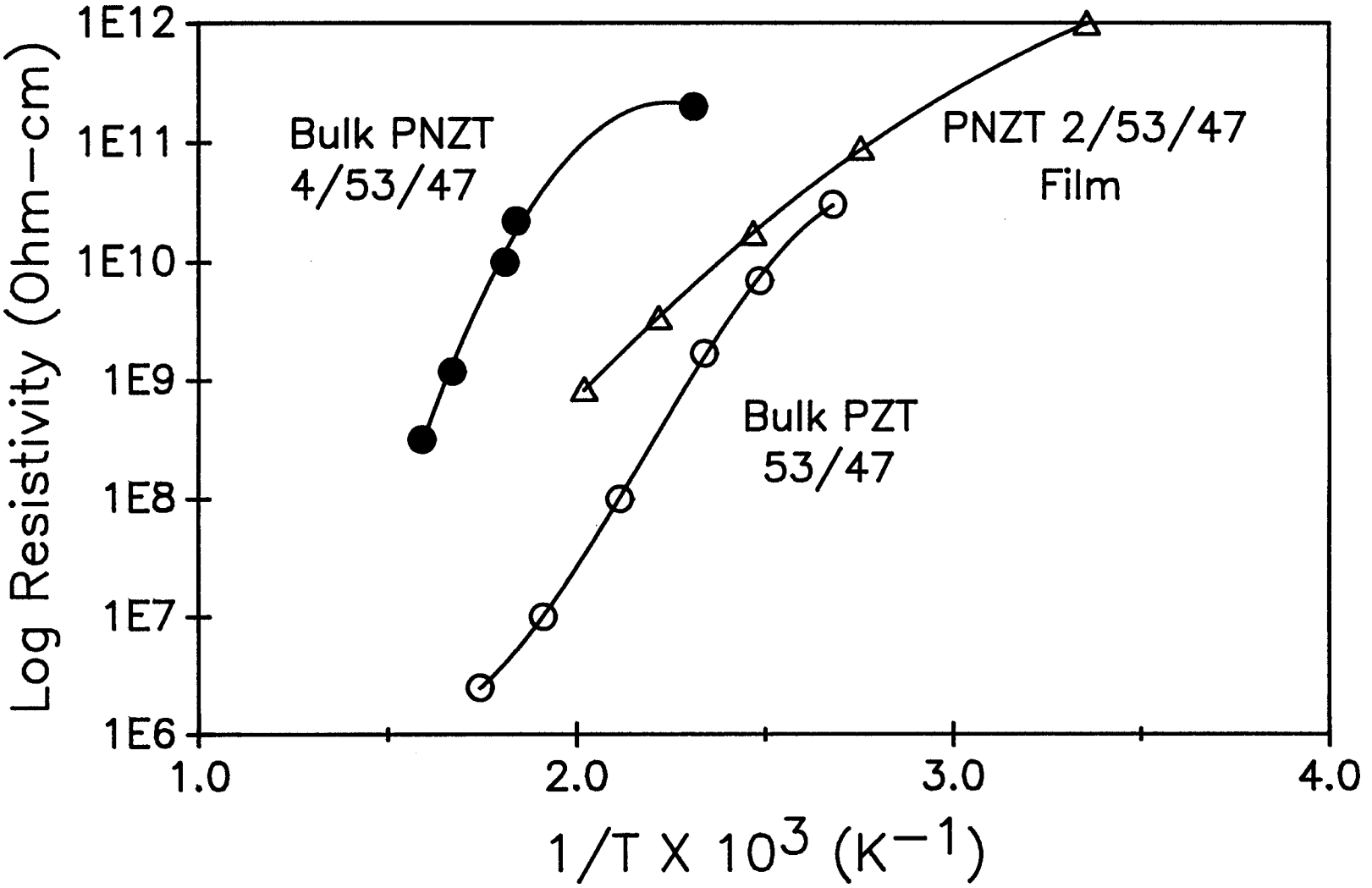
Figure 3. Resistivities of PZT film with 2 at% niobium addition are comparable to bulk PZT ceramics.

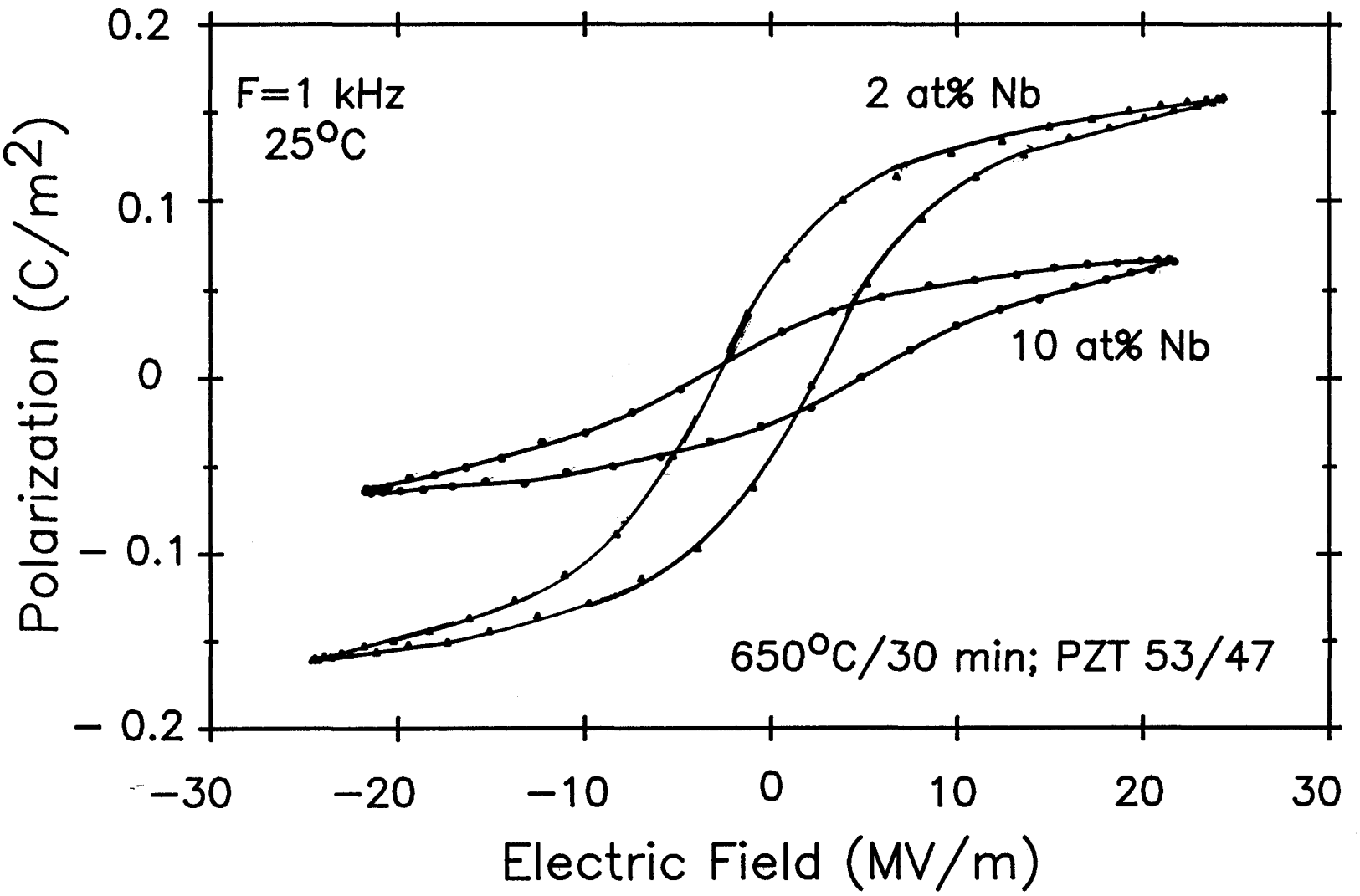
Figure 4. PZT 53/47 film with 2 at% Nb addition has better ferroelectric properties than PZT 53/47 film with 10 at% Nb addition.

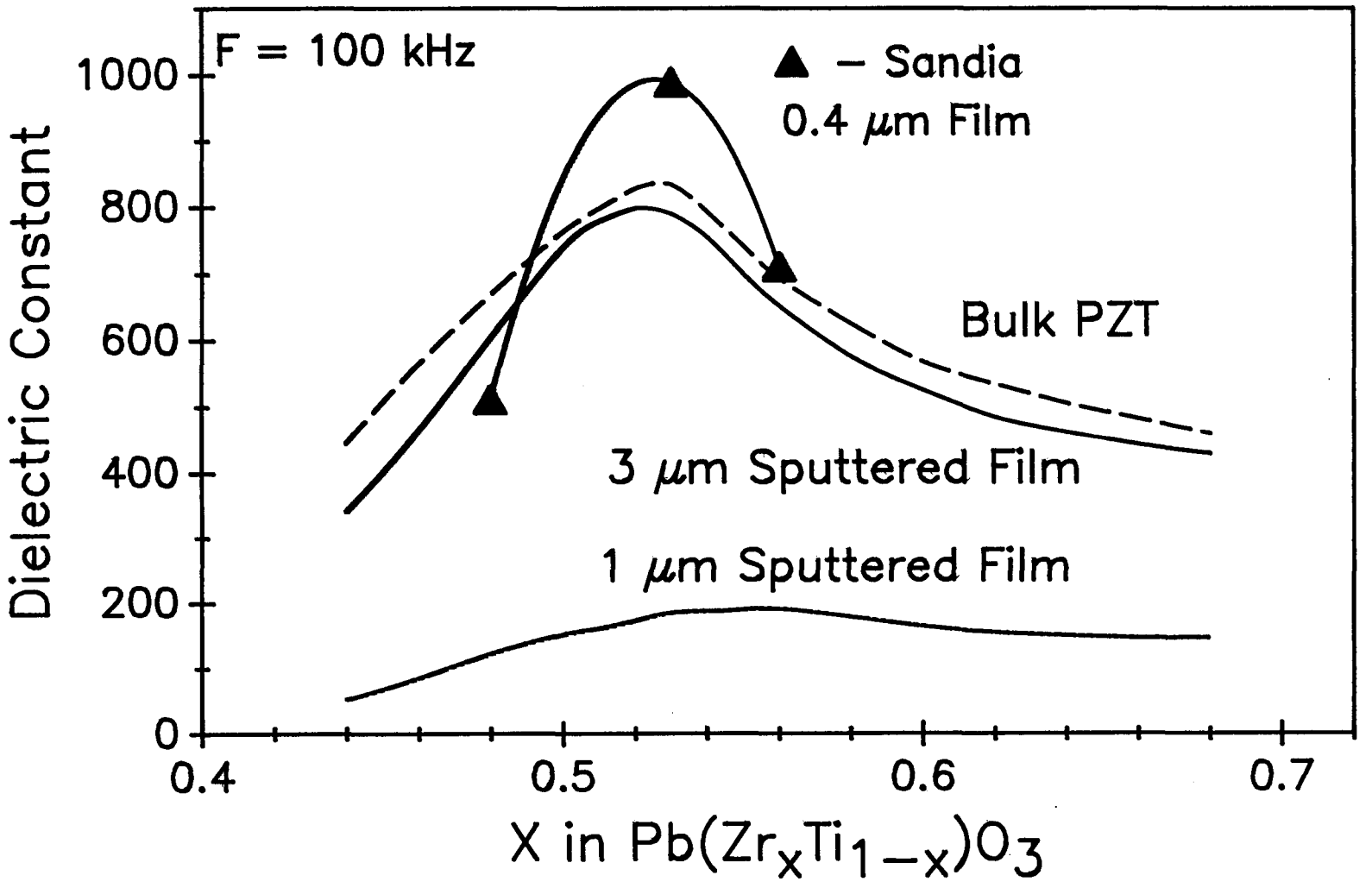
Figure 5. Chemically prepared PNZT films and bulk PZT ceramics show similar dielectric constant behavior as a function of Zr/Ti ratio.


Air
10°C/min
Pyrochlore
Crystallization
TGA
Perovskite
Conversion
DTA
Temperature Difference (°C)
Weight (%)
Temperature (°C)
15
10
5
0
100
90
80
70
60
50
0
200
400
600
800
General V2.2A DuPont 9900


PE -- Perovskite
PY -- Pyrochlore
PE
Pt
PE
PE
PE
PE
PE
645°C/30 minutes
610°C/30 minutes
570°C/30 minutes
PY
PY
PY
PY
PY
PY
INTENSITY (CPS)
*10
0.
49.
99.
149.
199.
249.
299.
349.
399.
10.
15.
20.
25.
30.
35.
40.
45.
50.
55.
60.
TWO - THETA (DEGREES)


Log Resistivity (Ohm−cm)
1E12
1E11
1E10
1E9
1E8
1E7
1E6
1.0
2.0
3.0
4.0
1/T X 10³ (K⁻¹)
Bulk PNZT
4/53/47
PNZT 2/53/47
Film
Bulk PZT
53/47


F=1 kHz
25°C
2 at% Nb
10 at% Nb
650°C/30 min; PZT 53/47
Polarization (C/m2)
Electric Field (MV/m)
0.2
0.1
0
− 0.1
− 0.2
−30
−20
−10
0
10
20
30


F = 100 kHz
▲ – Sandia
0.4 μm Film
Bulk PZT
3 μm Sputtered Film
1 μm Sputtered Film
Dielectric Constant
1000
800
600
400
200
0
0.4
0.5
0.6
0.7
X in Pb(ZrxTi1–x)O3