CONF-890421--5

SAND--89-0951C

DE89 010862

Ferroelectric Potassium Niobate Thin Films

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ABSTRACT

We report on the first ferroelectric measurements of chemically prepared $KNbO_3$ thin films. Polycrystalline $KNbO_3$ thin films were fabricated by dip coating substrates with methanolic solutions of potassium hydroxide and niobium ethoxide. Perovskite $KNbO_3$ was obtained for both bulk gels and films by using 800°C firing treatments. For films, the intermediate temperature processing schedule was critical for the complete conversion of low temperature phases to perovskite $KNbO_3$. Raman spectroscopy and X-ray diffraction analyses confirmed that properly processed films possessed the orthorhombic distortion of the perovskite structure at room temperature. In response to a 1 kHz, sinusoidal field of 300 kV/cm amplitude, we measured the following ferroelectric properties: 1) a remanent polarization of 4.5 $\mu C/cm^2$, 2) a spontaneous polarization of 8.3 $\mu C/cm^2$, and 3) a coercive field of 55 kV/cm.

INTRODUCTION

Potassium niobate thin films are of considerable interest for integrated optic device miniaturization and high speed optoelectronic switching. Because $KNbO_3$ has large electrooptic coefficients (r_{33} = 64 pM/V, r_{42} = 380 pM/V) and relatively small dielectric constants (k_{33} = 55, k_{11} = 160), it is potentially the highest speed transverse electrooptic modulator material.[1,2] In addition to guided-wave optic and optical shutter applications, other potential optoelectronic applications for $KNbO_3$ include phase conjugation[3,4], second harmonic generation[5] and high speed infrared detection.[6] $KNbO_3$ thin films that are suitable for these optoelectronic applications must have the following properties: 1) be single phase perovskite, 2) be electrically insulating for large applied electric fields (> 200 kV/cm), 3) be ferroelectric (required for linear electrooptic coefficients), and 4) have low optical loss. Until now, no one has demonstrated that single phase perovskite $KNbO_3$ thin films with good ferroelectric properties can be made. In this paper, we report

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on the fabrication and electrical characterization of chemically prepared, single phase perovskite, ferroelectric $KNbO_3$ films.

Ferroelectric potassium niobate possesses the perovskite crystal structure and is orthorhombic (mm2) at room temperature.[7] An orthorhombic to tetragonal phase transition is observed at 225°C, and a Curie point of 435°C, corresponding to the tetragonal to cubic phase transition has been measured.[8] A thorough review of the dielectric, optical and piezoelectric properties of single crystal $KNbO_3$ was given by Wiesendanger.[9] Properties of polycrystalline $KNbO_3$ were reported by Egerton and Dillon,[10] although dense polycrystalline $KNbO_3$ ceramics were difficult to make. $KNbO_3$ ceramics, 90% of theoretical density, were fabricated using a thorough powder washing procedure and near-melt temperature (1054°C) sintering. Takahashi et al[11] fabricated roller quenched, 80 μm thick films of polycrystalline $KNbO_3$, but only measured a spontaneous polarization of 0.88 $\mu C/cm^2$.

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[12-15] using sintering temperatures 600°C below the sintering temperature for bulk PZT. Dosch[16] developed a process, using methanolic solutions of barium hydroxide and titanium isopropoxide, to fabricate barium titanate thin films 700°C below the densification temperatures required for mixed oxide bulk barium titanate. Amorphous barium titanate films of high dielectric strength (> 5 MV/cm) were fabricated. We have used a technique similar to the Dosch process for the fabrication of $KNbO_3$ thin films.

EXPERIMENTAL PROCEDURE

Potassium niobate solutions of controlled stoichiometry (K:Nb = 1) were synthesized by blending niobium ethoxide with dried methanol in a polyethylene beaker for 5 minutes under ambient conditions. Potassium hydroxide was also dissolved in dried methanol and then slowly added to the stirred ethoxide solution over a period of 30 to 60 minutes. The resulting stable solutions were stored in sealed containers and placed in dessicators. Bulk gels of potassium niobate were made by drying the solutions in air for two weeks or longer and then drying at 50°C for 12 hours.

Immediately before film deposition, the solutions were filtered (0.2 micron filter). Potassium niobate films were then deposited onto our substrates by dipcoating in a dry glove box (2% relative humidity). Our substrates consisted of 200 nm thick Pt films, dc sputter deposited at an approximate rate of 2 nm per minute, on 2.54 cm diameter, (0001) sapphire wafers. Typically, the Pt film substrates were immersed in a 0.5 molar solution and immediately removed at a controlled rate (10 inches per minute). An 80 nm thick $KNbO_3$ layer was obtained after firing. Higher concentration (1.0 molar) solutions were used to deposit thicker (290 nm) $KNbO_3$ layers on sapphire substrates with out Pt films. These 1.0 molar solutions can be used for the fabrication of 2 μm thick $KNbO_3$ thin films required for integrated optics.

A multiple deposition process was developed to produce $KNbO_3$ films of the desired thickness (400 nm) for ferroelectric measurements. After each deposition the sample was heat treated, and then the sample was again dipcoated and refired until the desired film thickness was obtained. Although heat treatments ranging from 300°C to 800°C were used between layers to remove organics and modify crystal structure, between layer heat treatments of 700°C or more were required to produce single phase perovskite $KNbO_3$. After the last layer was deposited, a final firing at temperatures ranging from 600°C to 1050°C was performed. For Pt film substrates, final firing temperatures below 800°C resulted in films with multiple phases; whereas, firing temperatures above 850°C resulted in degradation of the Pt film. Platinum film degradation made electrical measurements impossible. Typically, a heating rate of 3°C/min and a soak time of 4 hours was used for both the between layer and final firing treatments. Film thickness was measured by Rutherford backscattering and surface profilometry. For electrical measurements, an array of top electrode Pt dots, ranging from 0.5 to 1.0 mm in diameter, were sputter deposited onto the $KNbO_3$ thin films. We used a modified Diamant-Pepinsky bridge for the ferroelectric measurements of our films.

RESULTS AND DISCUSSION

Figure 1 depicts thermogravimetric (TGA) and differential thermal analyses (DTA) for bulk gels in air, using a 10°C/minute heating rate. Below 300°C, the gradual weight loss of approximately 12% and the corresponding DTA endotherm are most likely due to the removal of methanol. Although a relatively abrupt 3% weight loss is observed at 425°C, we believe the distributed DTA exotherm that occurs at approximately 450°C corresponds not only to removal of the organics from our gel, but crystallization of a low temperature phase (LT phase) of $KNbO_3$. This low temperature phase does not appear to be ferroelectric, and has been reported by Nasssau et al[17] for roller quenched $KNbO_3$ materials. Results from our high temperature X-ray diffraction experiments, which will be discussed later, indicate the 620°C exotherm corresponds to initial crystallization of perovskite $KNbO_3$. Complete conversion of the low temperature phase to cubic perovskite $KNbO_3$, for a 10°C/minute heating rate, occurs above 750°C. The small exotherm at 760°C in Figure 1 is evidence of this conversion. Although not shown in Figure 1, we have performed a sequence of DTA experiments on bulk gels at different heating rates to determine the onset of melting. Extrapolation of the melt temperature to zero heating rate, using linear regression analysis, yields a melt temperature of 1048.5±2°C for our gels. Melting temperatures for $KNbO_3$ of 1039°C[18] and 1091°C[19] have been reported. The higher melt temperature was attributed to higher purity materials.

Raman spectra of two potassium niobate gels that were pyrolyzed at 550°C and 900°C for 4 hours are shown in Figure 2. After pyrolysis, the gels were crushed and screened to produce gel particles that were used for the Raman investigations. For the bulk gel particles pyrolyzed at 550°C, the finite signal observed for Raman shifts greater than 1200 cm^{-1} indicates a trace amount of carbon is still present in the gel. The strong band observed at approximately 900 cm^{-1} is characteristic of $Nb_6O_{19}^{8-}$ cluster formation that has been observed previously[20] in aqueous solutions. Gels that have been pyrolyzed at 900°C (Figure 2B) show no evidence of carbon bonding. The 900°C gel has Raman shifts in the 200 to 700 cm^{-1} range that are similar to the spectra measured for orthorhombic $KNbO_3$ single crystals.[21] Raman spectra for rhombohedral, orthorhombic, tetragonal and cubic perovskite $KNbO_3$ are readily distinguishable.

Figure 3a shows X-ray diffraction patterns taken at 450°C, 500°C, 650°C, and 800°C for a bulk gel. A 10°C/min heating rate was used and approximately 6 minutes was required to perform the X-ray diffraction measurement at each temperature. The amorphous pattern shown for the gel at 450°C is similar to the X-ray diffraction pattern taken at room temperature. For the 450°C pattern, the two well defined peaks at approximately 39° and 45° 2θ are due to the platinum heater underneath the gel. The broad intensity increases in the 450°C diffraction pattern correspond to the major peaks of a low temperature phase which is clearly evident in the X-ray diffraction pattern taken at 500°C. Nassau et al[17] have observed a similar phase in roller quenched potassium niobate that was detected at temperatures ranging from 390°C to 690°C. There may be a minor amount of another phase in the bulk gels at these intermediate temperatures. Although we detected the perovskite phase for temperatures as low as 600°C (see the 650°C diffraction pattern), complete conversion to the perovskite phase did not occur until 800°C for the 6 minute soak time. Bulk gels that were fired at 650°C for 4 hours were single phase perovskite by X-ray diffraction analysis.

Phase relationships as a function of temperature for films differed slightly from the behavior for gels. Room temperature X-ray diffraction patterns are shown in Figure 3b for two films with final firing temperatures of 700°C and 800°C, respectively. Except for the difference in the final firing temperature, the two films were processed identically. Each film consisted of 4 layers with a 700°C/4 hour heat treatment between each layer and both films were deposited on a sapphire/Pt film substrate. Although the film fired at 800°C appears to be single phase perovskite, the X-ray diffraction pattern for the film fired at 700°C shows evidence of other phases. For films fabricated with between layer process temperatures of less than 700°C, several phases were observed and conversion to perovskite $KNbO_3$ was not complete. For example, both the low temperature $KNbO_3$ phase and a potassium deficient $2K_2O.3Nb_2O_5$ phase were detected by X-ray analysis for a film fabricated using a 500°C process temperature between layers. After this film was heated to 750°C, the perovskite phase appears, but the film still contains multiple phases. Higher temperature heat treatments did not completely convert the film to the perovskite phase. We feel that between layer heat treatments are critical to the formation of ferroelectric, perovskite $KNbO_3$ thin films.

A scanning electron micrograph is shown in Figure 4 of the cross-sectional view of a $KNbO_3$ thin film that was fired at 800°C for 4 hours and was by X-ray diffraction analysis single phase perovskite. This ferroelectric film was deposited on a 200 nm thick Pt film/sapphire substrate and consisted of 4 layers. A 700°C/4h heat treatment was used between layers. Although the top surface of the film is uniform and relatively featureless, the micrograph of the film cross-section shows relatively equiaxed grains, ranging in size from 0.05 to 0.3 μm. Columnar growth is observed in the Pt film underneath the $KNbO_3$ layer, this growth morphology is typical of films deposited using slow sputter rates. Microstructures of films processed with between layer heat treatments ranging from 100°C to 600°C consisted of large 10 to 20 μm diameter crystallites embedded in a matrix of submicron perovskite $KNbO_3$. Electron microprobe analysis showed that these large crystals were potassium deficient.

The dielectric and ferroelectric properties of the $KNbO_3$ thin film in Figure 4 were in reasonable agreement with previous work. Egerton and Dillon[10] measured a dielectric constant of 430 and a dissipation factor of 0.02 for bulk polycrystalline $KNbO_3$. For our polycrystalline, ferroelectric $KNbO_3$ thin film, we measured the following electrical properties: 1) a dc resistivity of 10^{10} ohm-cm for an applied field of 30 kV/cm, 2) a dielectric constant of 300 and 3) a dissipation factor of 0.04 for a 10 kHz, 3 kV/cm applied field. Two ferroelectric hysteresis loops, measured for 1 kHz, sinusoidal applied fields of 100 and 300 kV/cm amplitude, are shown in Figure 5. No external resistance or capacitance compensation was used for these ferroelectric measurements. The hysteresis loop for the 100 kV/cm field is unsaturated. For the saturated hysteresis loop (300 kV/cm applied field), we measured a coercive field of 55 kV/cm, a remanent polarization of 4.5 $\mu C/cm^2$, and a spontaneous polarization of 8.3 $\mu C/cm^2$. Reported values of spontaneous polarization[22,23] for single crystal $KNbO_3$ range from 26 to 41 $\mu C/cm^2$. The lower value of spontaneous polarization for a polycrystalline thin film is not unexpected, and is in reasonable agreement with a spontaneous polarization of 4.4 $\mu C/cm^2$ measured[24] for hot-pressed $KTa_{0.6}Nb_{0.4}O_3$. Internal stress due to small grain size, piezoelectric clamping of grains, and complex domain structures are all factors that contribute to lower polarization values for polycrystalline thin films compared to single crystal materials.

SUMMARY

We have developed a sol-gel process, based on methanolic solutions of niobium ethoxide and potassium hydroxide, for the fabrication of $KNbO_3$ thin films and gels. Although undesirable, low temperature, potassium niobate phases were observed in many of our films, use of the appropriate thermal processing procedures resulted in single phase perovskite $KNbO_3$ by X-ray diffraction analysis. From our electrical measurements of these perovskite films, we obtained the following properties: 1) high electrical resistivity (10^{10} ohm-cm), 2) a dielectric constant of 300, 3) a dissipation factor of 0.04, 4) a coercive field of 55 kV/cm and 5) a spontaneous polarization of 8.3 $\mu C/cm^2$.

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Figures:

Figure 1. Thermogravimetric and differential thermal analyses of an alkoxide-derived $KNbO_3$ gel indicate small total weight loss and initial perovskite crystallization temperature of 620°C.

Figure 2. Raman spectra of potassium niobate bulk gels show: A) $Nb_6O_{19}^{8-}$ cluster formation with 550°C thermal treatment and B) orthorhombic symmetry after 900°C thermal treatment.

Figure 3. X-ray diffraction studies show that single phase perovskite $KNbO_3$ is produced using 800°C thermal treatments for: A) bulk gels and B) thin films.

Figure 4. Uniform grains, of approximately 0.1 micron grain size, are observed for the cross sectional view of a perovskite $KNbO_3$ thin film.

Figure 5. Ferroelectric hysteresis loops are measured for a $KNbO_3$ thin film with 1 kHz, applied fields of 100 and 300 kV/cm.

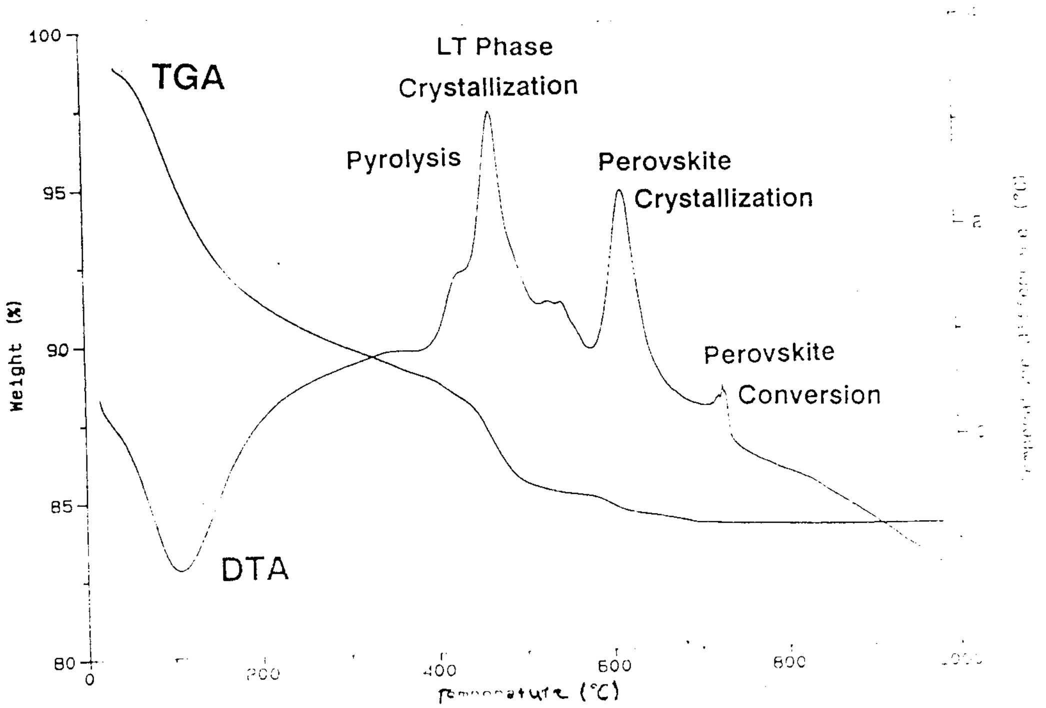
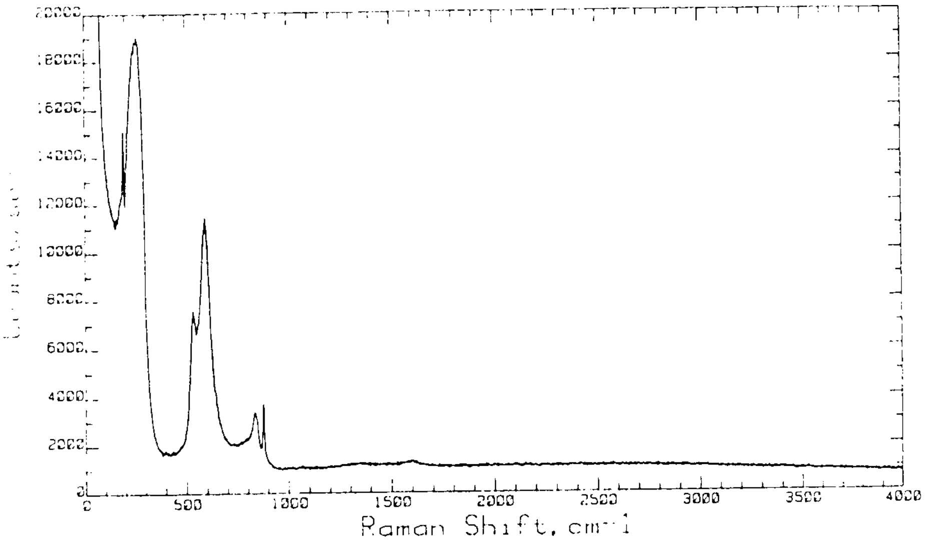
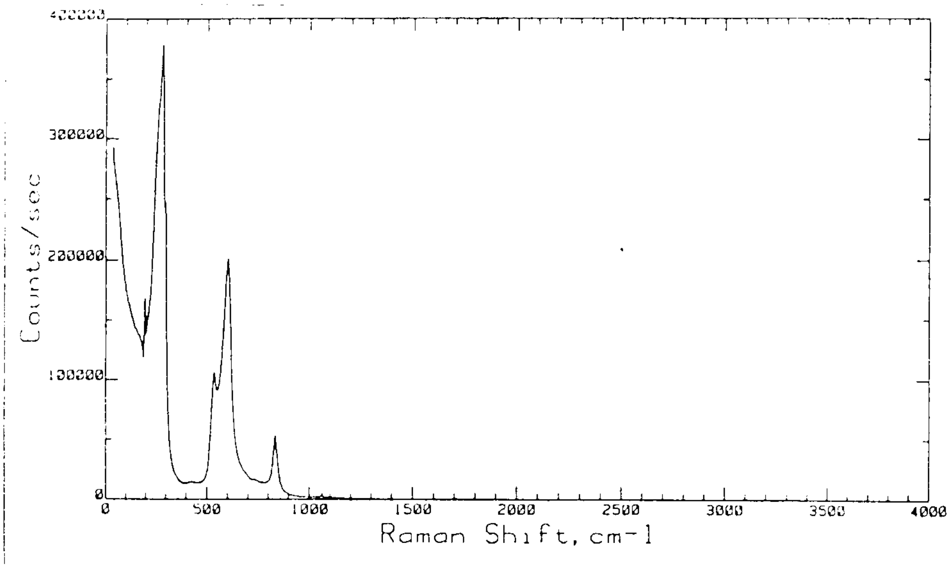

100
95
90
85
80
Weight (%)
TGA
DTA
LT Phase
Crystallization
Pyrolysis
Perovskite
Crystallization
Perovskite
Conversion
0
200
400
600
800
1000
Temperature (°C)

Figure 1



A) 550°C



B) 900°C

Figure 2

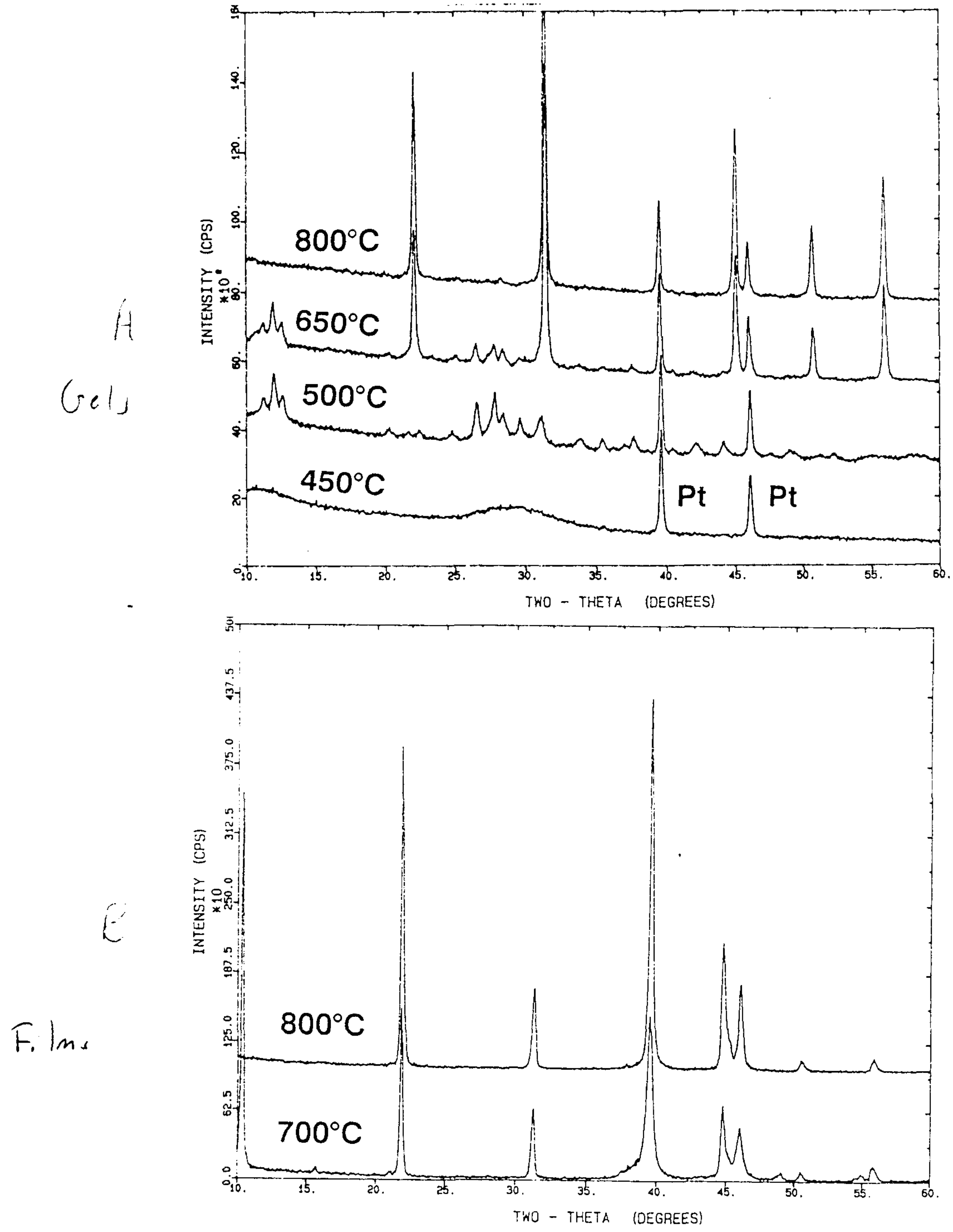

A
Gels
INTENSITY (CPS) *10
800°C
650°C
500°C
450°C
Pt
Pt
0.
20.
40.
60.
80.
100.
120.
140.
160
10.
15.
20.
25.
30.
35.
40.
45.
50.
55.
60.
TWO - THETA (DEGREES)
B
Films
INTENSITY (CPS) *10
800°C
700°C
0.0
62.5
125.0
187.5
250.0
312.5
375.0
437.5
500
10.
15.
20.
25.
30.
35.
40.
45.
50.
55.
60.
TWO - THETA (DEGREES)

Figure 3

25Kx

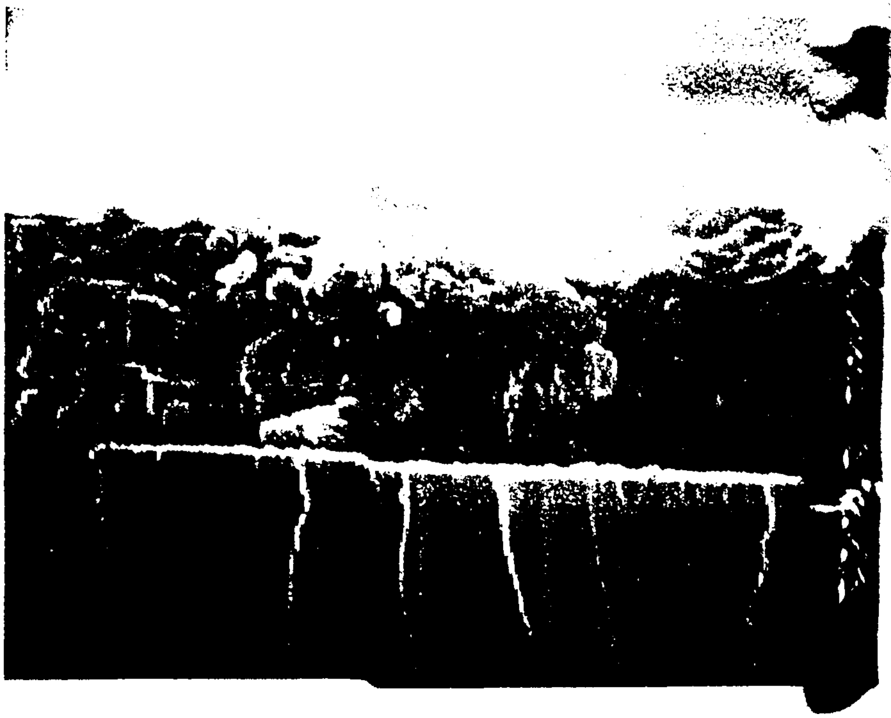


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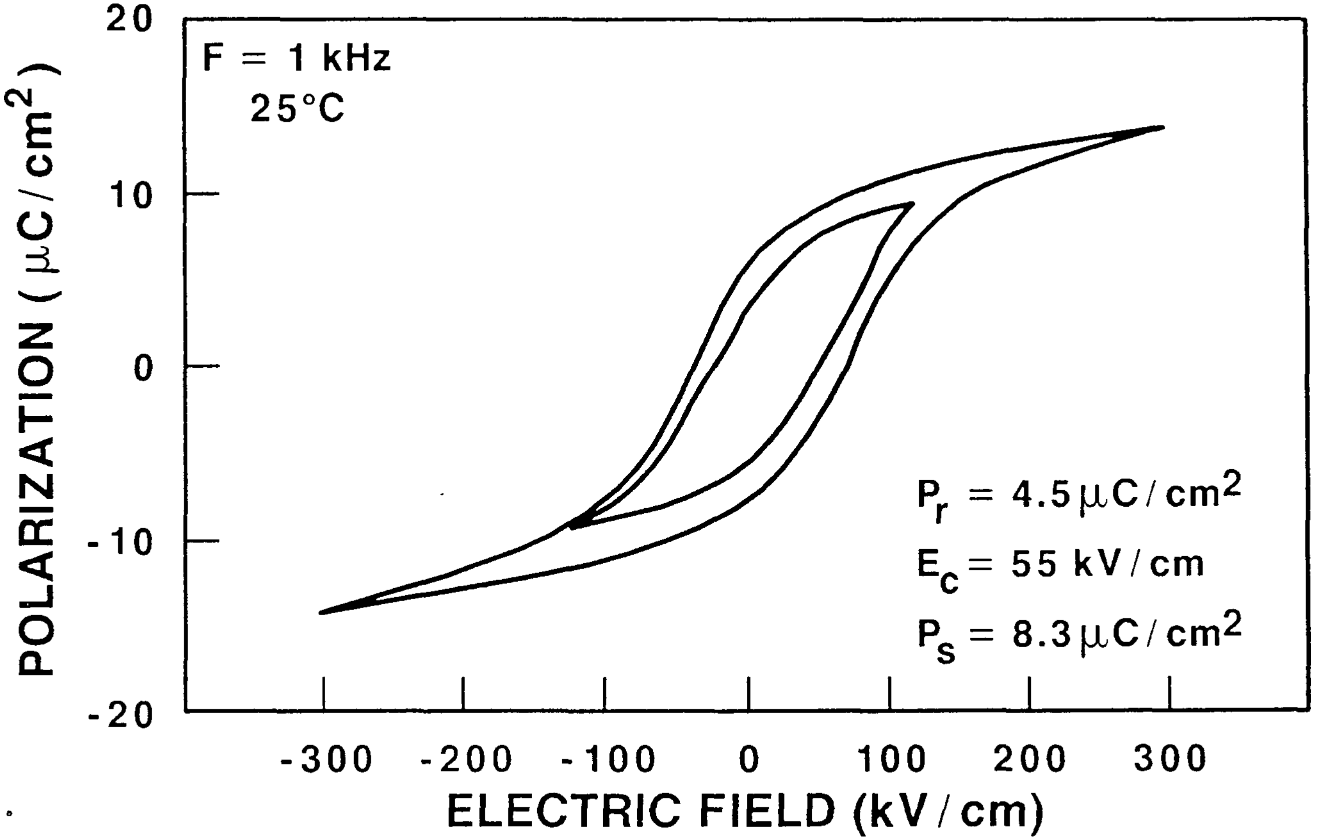
Figure.4

Figure 5

Sol-Gel $KNbO_3$ THIN FILMS ARE FERROELECTRIC
Pt / SAPPHIRE SUBSTRATE; 800°C / 4 HOURS



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