Structural and electrical characterization of lead metaniobate thin films deposited by pulsed laser ablation

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Abstract

Lead niobate thin films have been prepared by laser ablation, at different substrate temperatures (T_{dep}) and with different oxygen pressures (pO_2). For low deposition temperatures the films presented a rhombohedric-$PbNb_2O_6$ structural phase, with hysteresis cycles characteristic of a paraelectric. As T_{dep} increased the films started to develop an orthorhombic- $PbNb_2O_6$ structure that appeared at 400ºC and remained up to 600ºC. For low pO_2, a mixture of this phase and a lead deficient phase was present in the films. Increasing the oxygen pressure the lead deficient phase was strongly reduced and the films presented only the ferroelectric orthorhombic- $PbNb_2O_6$ structural phase.

RUNNING HEAD: Structure and electric characterization of lead niobate

INTRODUCTION

Lead metaniobate ($PbNb_2O_6$) is a good candidate for high temperature piezoelectric transducers due to its low mechanical quality factor Q, large anisotropy in the electromechanical coupling coefficient and high Curie temperature (570ºC) [1-6]. At temperatures above 1200ºC it has a tetragonal tungsten bronze structure. Upon cooling below 1200ºC it transforms to a rhombohedral form that is paraelectric at room temperature. The rhombohedral form is not far from cubic (α_{rh} = 93.9º) and has a perovskite like structure with alternate planes of PbO_3 and (vacant-site)O_3, in composition [7]. If the cooling through the 1200ºC-700ºC interval is fast, the tetragonal phase is retained down to 570ºC where it changes to a ferroelectric orthorhombic metastable structure [5]. The orthorhombic lattice parameters are a=17.51Å, b=17.51Å and c=7.73Å [7]

In ceramic form, dense $PbNb_2O_6$ is difficult to obtain by conventional techniques because of exaggerated grain growth due to the structural phase transformation from rhombohedral to tetragonal, during sintering [6]. In fact, when lead niobate is quenched from 1200ºC it experiences severe cracking, limiting its practical applications. To obtain the ferroelectric orthorhombic phase at reasonable cooling rates, various dopants such as $ZrTiO_4$ [5] and $Bi_4Ti_3O_{12}$ [8] have been used to stabilize the ferroelectric phase.

Also, when PbO reacts with Nb_2O_5, with different molar ratios, lead niobate compounds having pyrochlore related structures are formed when the lead content is higher than that of niobium [9]. On the other hand, when the niobium content is higher, lead niobate compounds crystallize with tungsten bronze type structures [10].

In thin film form, using sputtering [11] or sol-gel techniques [12], the ferroelectric orthorhombic led niobate phase can be stabilized at lower temperatures (450-900ºC [11,12]) as compared to ceramics. However, the stabilization of the ferroelectric orthorhombic phase is difficult due to the formation of non-ferroelectric phases during deposition. In order to

address this problem, lead metaniobate thin films have been prepared at different substrate temperatures and with different oxygen pressures, during deposition.

EXPERIMENTAL

The films were prepared by pulsed laser ablation on $Pt/TiO_2/SiO_2/(001)Si$ substrates. The depositions were done with a KrF excimer laser with wavelength λ=248nm, at a fluence of 1.5J/cm^2. The target was composed of a compressed lead niobate powder, sintered at 1200ºC during one hour. The X-ray diffraction spectrum measured on the target showed that it was polycrystalline and composed by PbN_2O_6 with a rhombohedral structure. A residual $Pb_3Nb_4O_{13}$ phase with a cubic pyrochlore structure was also observed. This phase has an excess of lead in its composition, as compared to $PbNb_2O_6$.

The oxygen pressure during film preparation (pO_2) was in the range 10^{-3}-2×10^{-2} mbar and the substrate temperature varied from room temperature to 600ºC. The distance from the target to the substrate (d_{ST}) was 2.3cm. The structural studies were performed by X-ray diffraction (XRD) and were carried out with a Philips PW-1710 diffractometer using Cu Kα radiation. The surface of the films was examined by scanning electron microscopy (SEM). The polarization versus electric field hysteresis loops were measured at room temperature, using a Sawyer-Tower circuit.

RESULTS AND DISCUSSION

Figure 1 show SEM micrographs obtained on samples deposited a) at 500ºC with $pO_2=8\times10^{-3}$mbar and b) at 600ºC with $pO_2=2\times10^{-2}$mbar.

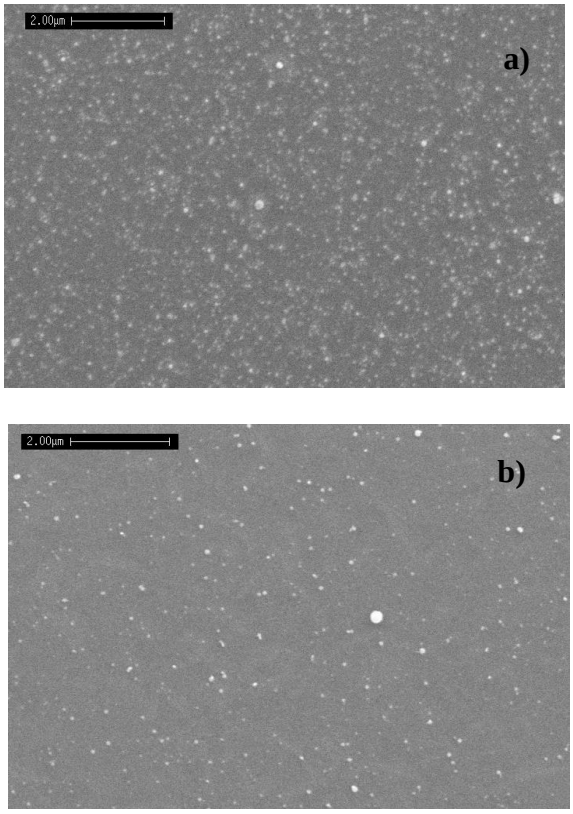

FIGURE 1: SEM micrographs of the surface of the films deposited with a) T_{dep}=500ºC and pO_2=8×10^{-3}mbar, and b) T_{dep}=600ºC and pO_2=2×10^{-2}mbar.

The films present a granular surface with average grain sizes, determined from the SEM micrographs, of 588 Å and 507 Å, respectively. For higher oxygen pressure we observe a less grainy surface and the films are denser. Inherent to the laser ablation technique is the appearance of small droplets (~ 0.5 - 2 μm) on the films surface. In our samples, the surface shows a low density of these droplets.

Figures 2a)-2c) show the X-ray diffraction spectra measured on films deposited at 400ºC, 500ºC and 600ºC, with lower oxygen pressures (4-8×10^{-3}mbar). Figures 2d)-2g) show the X-ray diffraction spectra measured on films deposited at 200ºC, 400ºC, 500ºC and 600ºC, with higher oxygen pressures (1-2×10^{-2}mbar). Figure 3 show and enlargement of the X-ray diffraction spectra of figure 2, in the 2θ angle range 20º-34º.

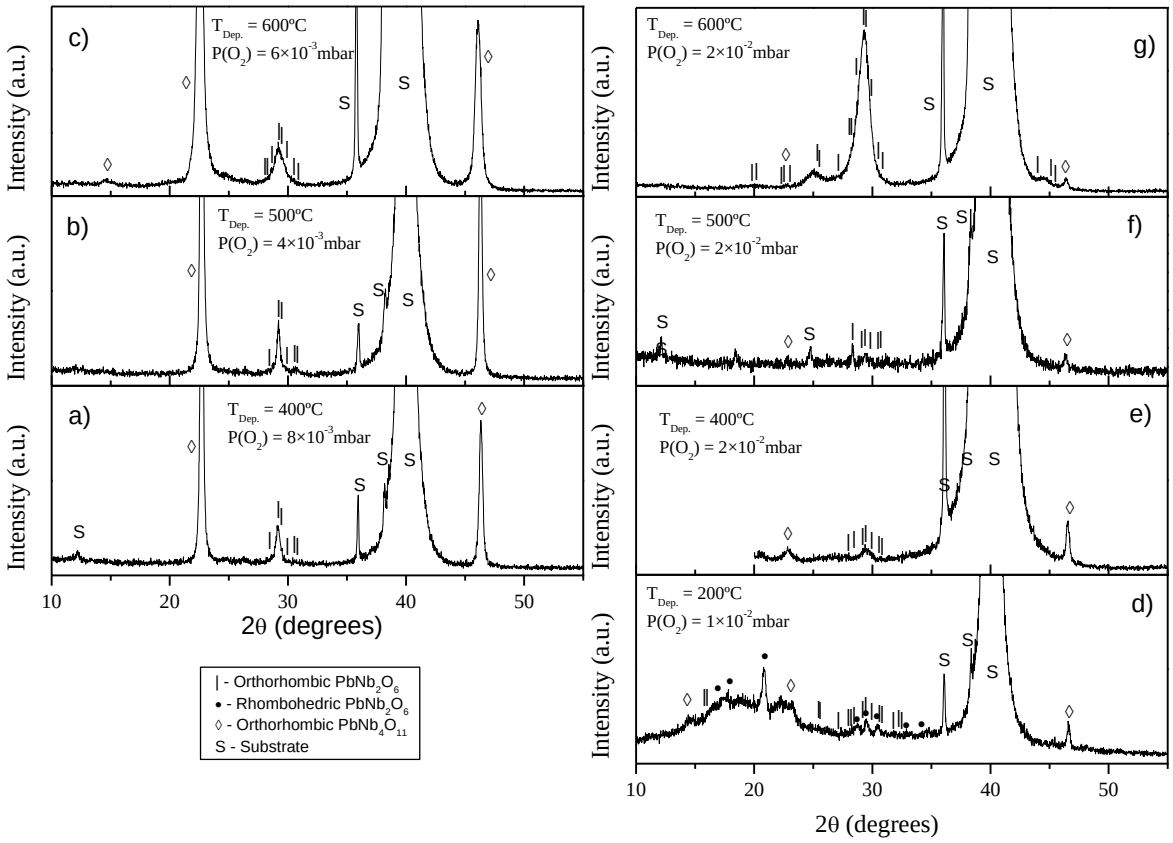

FIGURE 2: X-ray diffraction spectra measured on the samples deposited with substrate temperature in the range 400ºC-600ºC, and oxygen pressures a)-c) 4-8×10^{-3}mbar and d)-g) 1-2×10^{-2}mbar.

The vertical lines indicate the peak positions of the lead niobate orthorhombic-$PbNb_2O_6$ phase obtained in bulk samples. Open lozenges indicate the corresponding peak positions of a lead deficient $PbNb_4O_{11}$ phase with orthorhombic structure, which is also present in the films. Figures 2 and 3 indicate that their composition is a mixture of orthorhombic-$PbNb_2O_6$ or rhombohedric-$PbNb_2O_6$ with the lead deficient $PbNb_4O_{11}$ phase. The proportions of the different phases vary with deposition temperature and oxygen pressure.

For low deposition temperatures (T_{dep}~200ºC) the films present a polycrystalline rhombohedric-$PbNb_2O_6$ structural phase (fig. 2d). In figure 3, the black circles mark the peaks corresponding to the bulk rhombrohedral phase that exist in this angle interval. They

occur at 2θ angles 21.0º, 28.7º, 29.5º and 30.5º, and correspond to the lattice planes (021), (113), (300), and (122).

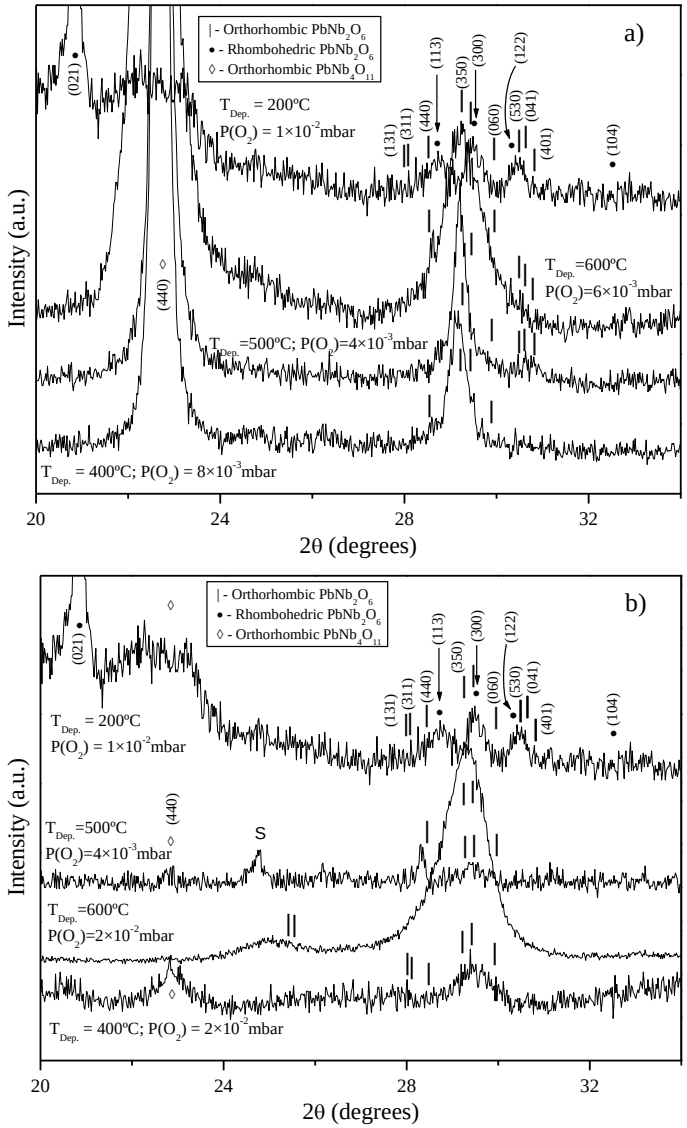

FIGURE 3: X-ray diffraction peaks for the films of figure 2 deposited with a) lower oxygen pressure and b) higher oxygen pressure, plotted on an expanded scale.

As T_{dep} increases above 400ºC the films start to develop an orthorhombic-$PbNb_2O_6$ structure that remains up to 600ºC. This is revealed by the appearance of peaks, located between the rhombohedric (113) and (300) directions, at a 2θ position between 28.6º and 30.1º, and of three peaks located between 2θ ~ 42º and 45º which are observed in the films deposited at 600ºC and correspond to the planes [660], [750] and [371]. On samples grown at

400ºC and 500ºC, with low oxygen pressure ($pO_2 \leq 8\times10^{-3}$ mbar), the peak at 2θ = 29.2º matches the orthorhombic-$PbNb_2O_6$ (350) lattice direction and its relative intensity indicate that the films have a (350) preferential orientation. For films grown at 600ºC with lower oxygen pressure the shape of the peak occurring near 29.2º indicates that it is a superposition of multiple peaks. A fit with multiple gaussian functions overlapping each other, gave the positions 29.2º, 29.5º and 30.0º, which are consistent with the bulk orthorhombic-$PbNb_2O_6$ peak positions of the (113), (350) and (300) directions shown in figure 3a). In samples grown with higher oxygen pressures, these three peaks are always present indicating a more polycrystalline structure, and the absence of a clear preferential growth direction. The X-ray diffraction coherence length for the orthorhombic-$PbNb_2O_6$ phase was determined from the (350) peak by using the Scherrer equation [13]. The values obtained on the deposited films were used as a measure of their grains size and were found to be in the range 200-650 Å, as shown in figure 4. They are consistent with values determined by direct observation in the SEM.

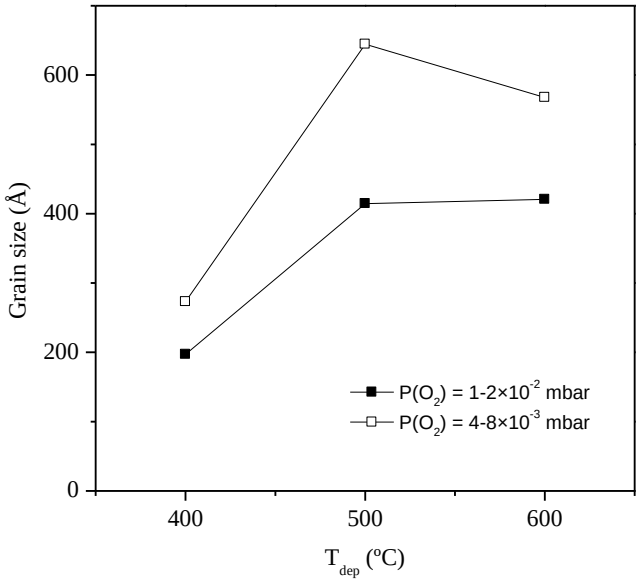

FIGURE 4: Grain size of the orthorhombic lead niobate $PbNb_2O_6$ phase, determined from the (350) peak width.

The average grain size increases with increasing deposition temperature and is smaller on samples deposited with higher oxygen pressures, due to the more polycrystalline structure of these films.

Figure 5 shows the relative intensity between the (350) peak of the orthorhombic-$PbNb_2O_6$ phase and the (440) peak of the lead deficient $PbNb_4O_{11}$ phase.

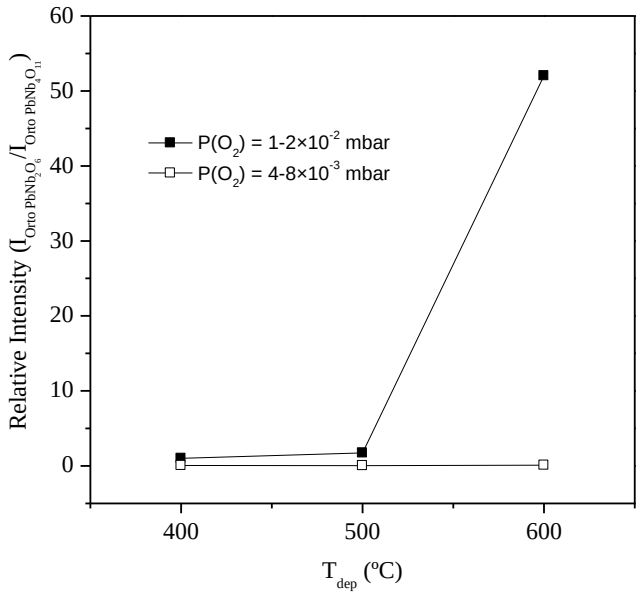

FIGURE 5: Relative intensity of the (350) peak of the orthorhombic $PbNb_2O_6$, and (440) of the orthorhombic $PbNb_4O_{11}$, as a function of temperature.

For lower oxygen pressures, the relative intensity rises from 0.06 at T_{dep}=400ºC to 0.1 for T_{dep}=600ºC indicating that the lead deficient phase in fact dominates the composition of these films. On the other hand, by increasing the oxygen pressure, the relative intensity strongly increases (from 1 at T_{dep}=400ºC to 52 at T_{dep}=600ºC), so that mainly the orthorhombic-$PbNb_2O_6$ form composes the films and only a residual lead deficient phase is observed in the X-ray diffraction spectra (figure 2). Thus, the increase of the oxygen pressure during deposition favors the formation of the orthorhombic-$PbNb_2O_6$ phase, as compared to the lead deficient $PbNb_4O_{11}$.

In the pressure range that was used during film deposition (4×10^{-3} mbar to 2×10^{-2} mbar) we are in a regime where the plume created when the laser interacts with the target has

a length (~3 cm for 2×10^{-2} mbar [14-16]) that is of the order, or higher than, the distance from the target to the substrate (d_{ST}=2.3cm). So the incident flux on the substrate is not thermalized and re-sputtering should be approximately the same in all the pressure range used.

Assuming that the plume, is mainly formed by atomic species (Pb and Nb) and considering a simple scattering model based on hard-spheres [14], it is possible to estimate the mean free path (λ) of Pb or Nb atoms in O_2 according to the expression:

$$\lambda = \frac{k_B T}{\pi P d^2} \qquad (1)$$

where k_B is the Boltzmann constant, T is the temperature of the background O_2 gas atmosphere, P is the gas pressure, and $d = r_i + r_{O_2}$ is the impact parameter (r_i and r_{O_2} being the radii of the species *i* (Pb or Nb) and O_2). To calculate the mean free paths, the values of the atomic radii of Pb, Nb, and O_2 that were used were [14,17]: r_{O_2} =1.8Å, r_{Pb}=1.54Å, and r_{Nb}=1.98Å. Their atomic masses are [17] m_{Pb}=207 and m_{Nb}=93.

In the pressure region $4\text{-}8\times10^{-3}$ mbar, the mean free paths of Nb and Pb (λ_{Nb}= 2.1cm and λ_{Pb}=1.8cm for T_{dep}=400ºC, and λ_{Nb}= 3.2cm and λ_{Pb}=2.6cm for T_{dep}=600ºC) are of the order, or higher, than the distance from the target to substrate (d_{ST}=2.3cm). Then, the higher mean free path of Nb and the higher volatility of lead favor the formation of the lead deficient $PbNb_4O_{11}$ phase at lower oxygen pressures.

On the other hand, in the pressure region $1\text{-}2\times10^{-2}$ mbar the mean free paths of Pb and Nb (λ_{Nb}=0.8cm and λ_{Pb}=0.7cm for T_{dep}=400ºC, and λ_{Nb}= 1.2cm and λ_{Pb}=1.0cm for T_{dep}=600ºC) become much shorter than the distance from the target to the substrate. Then, the number of collisions that Nb and Pb atoms experience until they reach the substrate is high and the dominant effect that determines the relative amount of Pb and Nb in the deposited films is the masses [14]. Since $m_{Pb}>m_{Nb}$, the broadening of the angular distribution of Pb atoms arriving at the substrate is smaller than that of Nb. So, the relative number of atoms of

Pb traveling along the normal to the target will be higher. This then leads to a reduction of the lead deficiency in the films deposited at higher oxygen pressures, and to the stabilization of the orthorhombic-$PbNb_2O_6$ phase as shown in figure 5.

Figure 6 shows the polarization hysteresis cycles measured on the samples deposited with a) T_{dep}=200ºC and pO_2=8×10^{-3}mbar and b) T_{dep}=600ºC and pO_2=2×10^{-2}mbar.

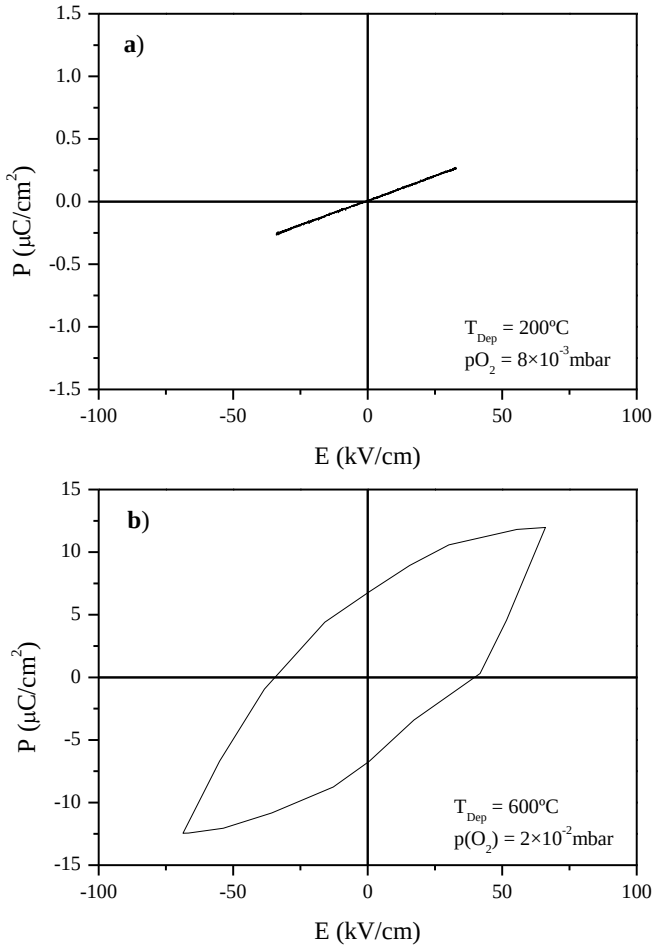

FIGURE 6. Polarization as a function of applied electric field, measured on the samples deposited with a) T_{dep}=200ºC and pO_2=8×10^{-3}mbar and b) T_{dep}=600ºC and pO_2=2×10^{-2}mbar.

For films deposited at lower temperature the polarization hysteresis loops present a linear dependence (fig. 6a), consistent with the paraelectric behaviour of the rhombohedral phase. On the other hand for the samples deposited at higher oxygen pressure and substrate temperature the cycles show a tendency towards saturation, as shown in figure 6b) for

T_{dep}=600ºC. Similar unsaturated loops have been observed in bulk lead metaniobate ceramics [4,6,7], and in thin films [11,12]. In the case of figure 6b) the remanent polarization (P_r) is 6.7μC/cm^2 and the coercivity E_c is 34kV/cm. The value of P_r is lower than the remanent polarization obtained on sol-gel films (12.3μC/cm^2) [12], and the polarization value is also lower than the 15μC/cm^2 obtained at 500kV/cm on lead niobate films deposited by sputtering and then annealed by pulsed thermal processing [11]. This is due to the residual lead deficient $PbNb_4O_{11}$ phase still present on the films deposited at higher oxygen pressures (pO_2=2×10^{-2} mbar) and substrate temperatures (T_{dep}=600ºC), as show in the X-ray diffraction spectrum of figure 2g).

CONCLUSIONS

Lead niobate thin films have been prepared by pulsed laser ablation at different oxygen pressures and substrate temperatures. For low oxygen pressures ($pO_2 \leq 8\times10^{-3}$mbar) they present an orthorhombic-$PbNb_2O_6$ structure mixed with a lead deficient phase with $PbNb_4O_{11}$ stoichiometry. By increasing the substrate temperature and oxygen pressure the lead deficient phase was strongly reduced so that for T_{dep}=600ºC and pO_2=2×10^{-2}mbar the orthorhombic-$PbNb_2O_6$ phase dominated the films composition. Hysteresis cycles measured on these films presented ferroelectric hysteresis loops that do not show saturation, as already observed in bulk lead metaniobate ceramics and thin films.

References

[1] - Ray S., Gunther E., and Ritzhaupt-Kleissl H.J.: Manufacturing and characterization of piezoceramic lead metaniobate $PbNb_2O_6$. J. Mater. Sci. Vol. **35**, 6221 (2000)

[2] - Eyraud P., Eyraud L., Gonnard P., Noterman D., and Troccaz M.: Electromechanical properties of $PbNb_2O_6$ and $PbTiO_3$ modified ceramics elaborated by a coprecipitation

process. *Proceedings of the Sixth IEEE International Symposium on Applications of Ferroelectrics*, New York: IEEE (1986)

[3] - Allahverdi M., Hall A., Brennan R., Ebrahimi M.E., Marandian Hagh N., and Safari A.: An overview of rapidly prototyped piezoelectric actuators and grain-oriented ceramics. J. Electroceram. **8**, 129 (2002)

[4] - Goodman G.: Ferroelectric properties of lead metaniobate. J. Am. Ceram. Soc. **36**, 368 (1953)

[5] - Moulson A.J., and Herbert J.M.: Electroceramics. London: Chapman and Hall (1990)

[6] - Sung Lee H., and Kimura T.: Effects of microstructure on the dielectric and piezoelectric properties of lead metaniobate. J. Am. Ceram. Soc. **81**, 3228 (1998)

[7] - Herbert J.M.: Ferroelectric transducers and sensors. London: Gordon and Breach, (1985)

[8] – Subbarao E.C. and Hrizo J.: J. Am. Ceram. Soc. **45**, 528 (1962)

[9] - Sreedhar K. and Mitra A.: Formation and transformation of cubic lead niobate pyrochlore solid solutions. J. Am. Ceram. Soc. **82**, 1070 (1999)

[10] - Brusset H., Mahé R., and Aung Kyi U.: Etude de niobates divalents binaires et ternaires a l'etat solide. Mat. Res. Bull. 7, 1061 (1972)

[11] - Vasant Kumar C.V.R., Sayer M., and Pascual R.: Ferroelectric lead niobate films by pulsed thermal processing. Appl. Phys. Lett. **60**, 2207 (1992)

[12] - Xue J.M., Ezhilvalavan S., Gao X.S., and Wang J.: Strontium titanate doped lead metaniobate ferroelectric thin films. Appl. Phys. Lett. **81**, 877 (2002)

[13] - Cullity B.D.: Elements of X-Ray Diffraction. Reading MA: Addison-Wesley, (1978)

[14] - Gonzalo J., Gomez San Roman R., Perrière J., Afonso C.N., Perez Casero R.: Pressure effects during pulsed-laser deposition of barium titanate thin films. Appl. Phys. A **66**, 487 (1998)

[15] Kools, J.C.S.: Monte Carlo simulations of the transport of laser-ablated atoms in a diluted gas. J. Appl. Phys. **74**, 8401 (1993)

[16] Geohegan, D.B.: Fast intensified-CCD photography of $YBa_2Cu_3O_{7-x}$ laser ablation in vacuum and ambient oxygen. Appl. Phys. Lett. **60**, 2732 (1992).

[17] - CRC Handbook of chemistry and physics 66^{th} edition, R.C. Weast (Editor), Crc Press Inc (1985)