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

F. Cardoso[a], B.G. Almeida[a], P. Caldelas[a], J.A. Mendes[b]

Departamento de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga

Portugal

[a]bernardo@fisica.uminho.pt, [b]jamendes@fisica.uminho.pt

Abstract. The ferroelectric polymorph of lead metaniobate ($PbNb_2O_6$) presents an orthorhombic structure that is metastable at room temperature. This phase is obtained by quenching from high temperature. The fabrication of lead niobate thin films with this orthorhombic form has been reported to be difficult due to the presence of phases with the rhombohedric form or other non-stoichimetric phases. In this work, lead niobate thin films have been prepared by laser ablation, at different oxygen pressures and with different substrate temperatures. Their structure was studied by X-ray diffraction and their surface was examined by scanning electron microscopy (SEM). The results show that for low deposition temperatures the films presented a rhombohedric-$PbNb_2O_6$ structural phase. As T_{dep} increases the films started to develop an orthorhombic- $PbNb_2O_6$ structure that appeared at 400ºC and remains up to 600ºC. For lower oxygen pressure during deposition, a mixture of this phase and other orthorhombic lead deficient phases are present in the films. On the other hand, by increasing the oxygen pressure the lead deficient phases are strongly reduced and the films present only the orthorhombic- $PbNb_2O_6$ structure.

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) [1-5]. 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. 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 structure [4].

In ceramic form, dense $PbNb_2O_6$ is difficult to obtain by conventional ceramic techniques because of exaggerated grain growth due to the structural phase transformation from rhombohedral to tetragonal, during sintering [5]. In fact, when lead metaniobate is quenched from 1200ºC it experiences severe cracking, limiting its practical applications.

In thin film form, using sputtering [6] or sol-gel techniques [7], the stabilization of the ferroelectric orthorhombic phase is difficult due to the formation of non-ferroelectric phases during deposition. In particular, the presence of rhombohedral form as well as pyrochlore related structures with different compositions hinders the formation of the ferroelectric phase. In order to address this problem, lead metaniobate thin films have been prepared by laser ablation at different oxygen pressures and at different substrate temperatures. The determination of phases formed during deposition was performed by X-ray diffraction.

Experimental

The films were prepared by pulsed laser ablation on $Pt/TiO_2/SiO_2/Si(001)$ substrates. These substrates were obtained from Neyco Ltd and were chosen since Pt is chemically stable in a high processing temperature and can be used as a bottom contact in dielectric measurements. 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 metaniobate powder, sintered at 1200°C during one hour. The X-ray diffraction spectrum measured on the target shows that it was polycrystalline and composed by lead niobate with a PbN_2O_6 rhombohedral structure. A residual $Pb_3Nb_4O_{14}$ phase with a cubic pyrochlore structure was also observed.

The oxygen pressure $P(O_2)$ during film preparation was in the range 10^{-3}-2×10^{-2} mbar and the substrate temperature varied from room temperature to 600°C. The X-ray diffraction (XRD) structural studies 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).

Discussion

Figure 1 show SEM micrographs obtained on samples deposited a) at 500°C with $P(O_2)$=8$\times10^{-3}$mbar and b) at 600°C with

Fig. 1: SEM micrographs of the surface of the films deposited with a) T_{dep}=500°C and $P(O_2)$=8$\times10^{-3}$mbar, and b) T_{dep}=600°C and $P(O_2)$=2$\times10^{-2}$mbar.

$P(O_2)$=2$\times10^{-2}$mbar. The films present a granular surface with average grain sizes 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.

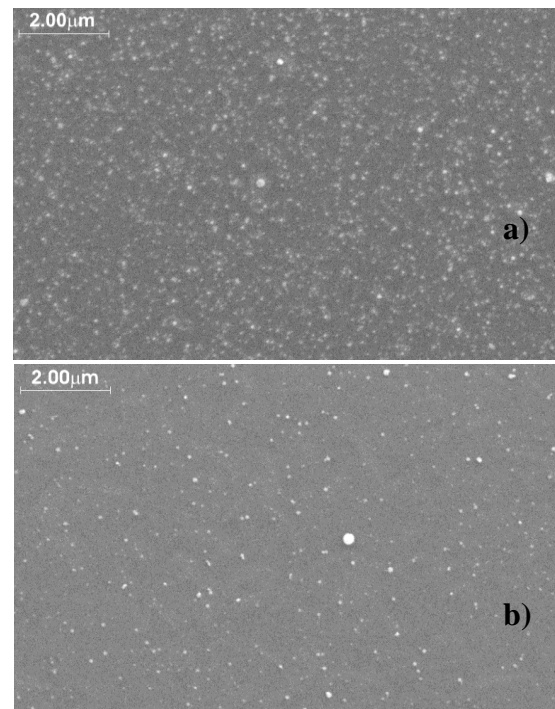Figures 2a)-2c) show the X-ray diffraction spectra measured on films deposited at 400ºC, 500ºC and 600ºC, with low oxygen pressures. Figures 2d)-2g) show the X-ray diffraction spectra measured on films deposited at 200ºC, 400ºC, 500ºC and 600ºC, with higher oxygen pressures.
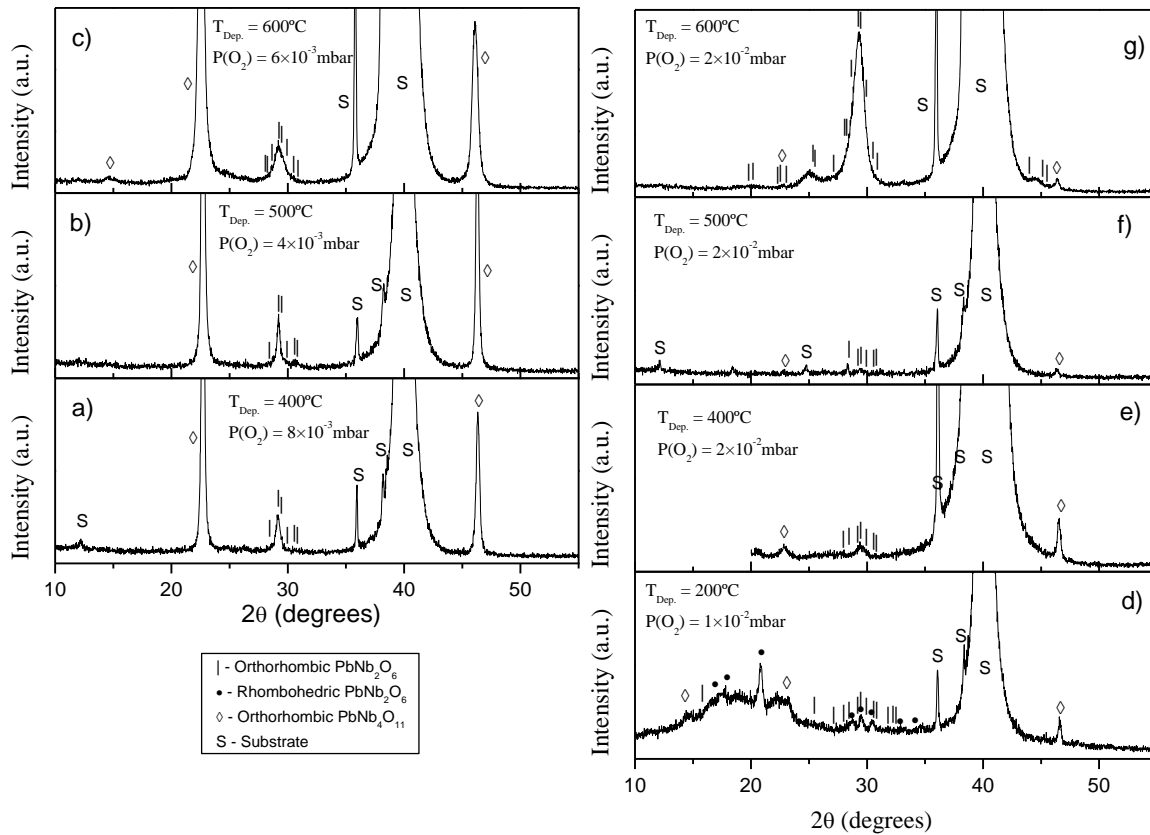

Fig. 2: X-ray diffraction spectra measured on the samples deposited with substrate temperature in the range 400ºC-600ºC, and oxygen pressures a)-c) 4-8×10^{-3}mbar and d)-g) 1-2×10^{-2}mbar.

The vertical lines indicate the peak positions of the lead niobate orthorhombic phase obtained in bulk samples. The open lozenges indicate the corresponding peak positions of the lead deficient $PbNb_4O_{11}$ phase with the orthorhombic structure. Figure 3 show and enlargement of the X-ray diffraction spectra of figure 2, in the 2θ angle range 20º-34º. The angular position and
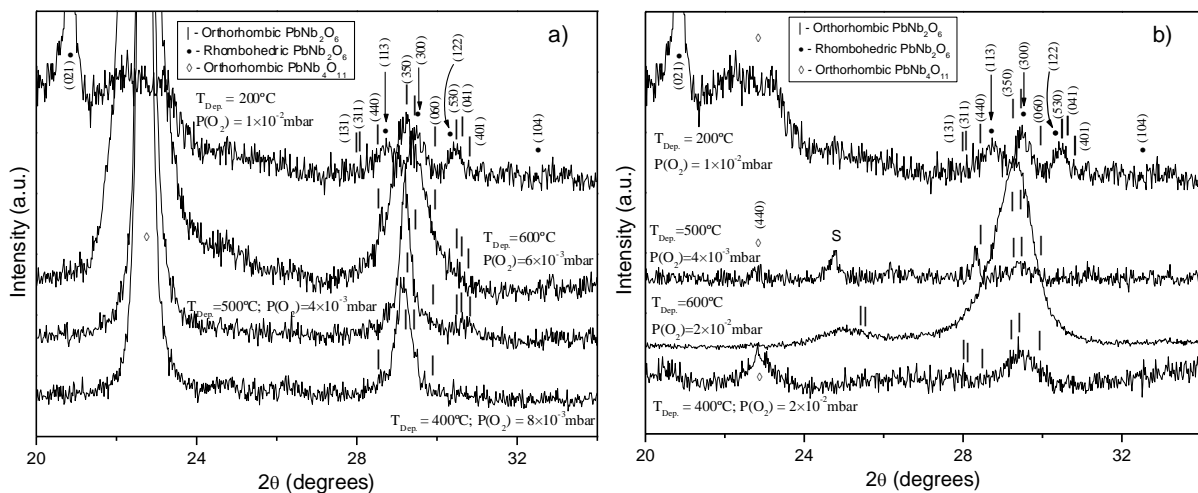

Fig. 3: X-ray diffraction peaks for the films deposited with a) lower oxygen pressure and b) higher oxygen pressure, plotted on an expanded scale.

relative intensity of the substrate peaks is similar in all the films, and the SEM micrographs (fig. 1) do not present holes or hillocks that tend to be produced on them at higher temperatures (>650°C) [8]. Thus, the substrates do not show surface degradation upon film deposition. Figures 2 and 3 indicate that the films 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 ($T_{dep} \sim 200°C$) the films presented a polycrystalline rhombohedric-$PbNb_2O_6$ structural phase. 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 21.0°, 28.7°, 29.5° and 30.5°, and correspond to the lattice planes (021), (113), (300), and (122).

As T_{dep} increases the films start to develop an orthorhombic-$PbNb_2O_6$ structure that appears at 400°C and remains up to 600°C. This is revealed by the appearance of peaks, located between the rhombohedric (113) and (300) peaks, at a 2θ position between 28.6° and 30.1° and of three peaks located between $2\theta \sim 42°$ and 45° which are well observed in the films deposited at 600°C and correspond to the planes [660], [750] and [371]. On samples grown at 400°C and 500°C, with lower oxygen pressure, the peak at $2\theta = 29.2°$ matches the (350) lattice direction and its relative intensity indicate that the films have a (350) preferential orientation. For the films grown at 600°C with lower oxygen pressure the shape of the peak occurring near 29.2° indicates that it is a superposition of multiple peaks. A fit with multiple gaussian peak functions, overlapping each other, gave the positions 29.2°, 29.5° and 30.0°, which are consistent with the bulk 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 grain sizes for the orthorhombic-$PbNb_2O_6$ phase were determined from the (350) peak by using the Scherrer equation [9]. Their values were found to be in the range 200-650 Å, as shown in figure 4, and are consistent with values determined by direct observation in the SEM. The average grain size increase with increasing deposition temperature and are smaller on samples deposited with higher oxygen pressures, due to the more polycrystalline structure of these films.
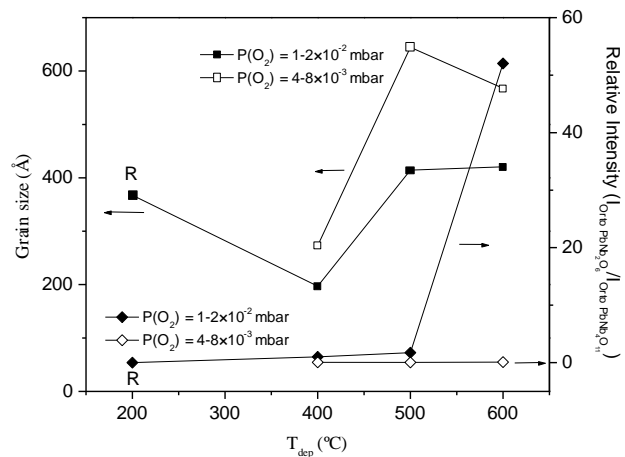

Fig. 4: Relative intensity of the peak (350) of the orthorhombic $PbNb_2O_6$, and (440) of the orthorhombic $PbNb_4O_{11}$, as a function of temperature. Also shown is the grain size of the orthorhombic lead niobate $PbNb_2O_6$ form. The points marked with an R belong to samples with the $PbNb_2O_6$ rhombohedral structure.

Figure 4 also 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. 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 goes from 1.0 in the samples deposited at 400º to 52 for the samples deposited at 600ºC. Thus, at intermediate temperatures the proportion of the orthorhombic-$PbNb_2O_6$ phase is similar to the proportion of the lead deficient phase, as shown in figure 4, but it increases so that at T_{dep}=600ºC dominates. At this deposition temperature the films are composed mainly by the orthorhombic-$PbNb_2O_6$ form and only a residual lead deficient phase is observed in the X-ray diffraction spectra.

Conclusions

Lead niobate thin films have been prepared by pulsed laser ablation at different oxygen pressures and substrate temperatures. For low oxygen pressure they present an orthorhombic-$PbNb_2O_6$ structure mixed with $PbNb_4O_{11}$ lead deficient phase. Increasing the substrate temperature and oxygen pressure the lead deficient phase was strongly reduced so that for T_{dep}=600ºC and $P(O_2)$=2×10^{-2}mbar the orthorhombic-$PbNb_2O_6$ phase dominated the films composition.

References

[1] - S. Ray, E. Gunther, and H.J. Ritzhaupt-Kleissl: J. Mater. Sci. Vol. 35 (2000), p. 6221

[2] - P. Eyraud, L. Eyraud, P. Gonnard, D. Noterman, and M. Troccaz: *Proceedings of the Sixth IEEE International Symposium on Applications of Ferroelectrics*, (IEEE, New York 1986)

[3] - M. Allahverdi, A. Hall, R. Brennan, M.E. Ebrahimi, N. Marandian Hagh, and A. Safari: J. Electroceram. Vol. 8 (2002), p. 129

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

[5] - H. Sung Lee, and Toshio Kimura: J. Am. Ceram. Soc. Vol. 81 (1998), p. 3228

[6] - C.V.R. Vasant Kumar, M. Sayer, and R. Pascual: Appl. Phys. Lett. Vol. 60 (1992), p. 2207

[7] - J.M. Xue, S. Ezhilvalavan, X.S. Gao, and J. Wang: Appl. Phys. Lett. Vol. 81 (2002), p. 877

[8] - S. Y. Kweon, S. K. Choi, S. J. Yeom, and J. S. Roh: Jpn. J. Appl. Phys. Vol. 40 (2001) 5850

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