

## Structural Characterization and Ferroelectric Properties of Strontium Barium Niobate ( $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ ) Thin Films

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Received: November 26, 2000; Revised: April 1, 2001

Strontium barium niobate (SBN) thin films of good quality were deposited on Pt/Ti/SiO<sub>2</sub>/Si substrate using a polymeric resin containing metallic ions. Films were crystallized at different temperatures and for different duration of time. The structure of these films was studied using X-ray diffraction. The coexistence of SrNb<sub>2</sub>O<sub>6</sub> (SN) and SBN was observed in films crystallized at 700 °C. The amount of SN decreases when the crystallization time increases. Ferroelectric properties were determined for films crystallized at 700 °C for 1 and 5 h. For SBN film crystallized at 700 °C for 1 h, the remanent polarization ( $P_r$ ) and the coercive field ( $E_c$ ) were 2.6  $\mu\text{C}/\text{cm}^2$  and 71.9 kV/cm, respectively. For the film crystallized at 700 °C for 5 h these parameters were  $P_r = 1.1 \mu\text{C}/\text{cm}^2$  and  $E_c = 50.5 \text{ kV}/\text{cm}$ .

**Keywords:** thin films, SBN, tungsten bronze structure

### 1. Introduction

Ferroelectric materials are an important class of materials whose main characteristic is the presence of a spontaneous polarization that can be changed with an external electric field. Ferroelectrics include titanates, zirconates, niobates and they can be classified by their structure type.

Fifty years ago, Magneli<sup>1</sup> deduced the tungsten bronze structure. The tungsten bronze family is one of several ferroelectric materials that includes niobates such as (Sr,Ba)Nb<sub>2</sub>O<sub>6</sub> (SBN), (Pb,Ba)Nb<sub>2</sub>O<sub>6</sub> (PBN) and (Pb,K)Nb<sub>2</sub>O<sub>6</sub> (PKN). An important representing of this family is the SBN ( $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ ), known by excellent pyroelectric coefficient<sup>2</sup>, piezoelectric<sup>3</sup> and electro-optic properties<sup>4,5</sup>. SBN presents a tetragonal or orthorhombic phase, depending of composition and temperature. A solid solution of SBN exists in the binary SrNb<sub>2</sub>O<sub>6</sub>-BaNb<sub>2</sub>O<sub>6</sub> system. Investigations using X-ray diffraction suggest a morphotropic phase boundary (MPB) around  $x = 0.25$ , which is characterized by the coexistence of the tetragonal

and orthorhombic phases<sup>6</sup>. SBN with  $x = 0.2$  present a tetragonal ferroelectric phase between 120 and 293 °C, below 120 °C present an orthorhombic phase and a tetragonal paraelectric phase above 293 °C.

The structure of SBN was studied by Jamieson *et al.*<sup>7</sup>, using X-ray diffraction. The tetragonal SBN structure consists of a framework of NbO<sub>6</sub> octahedra sharing corners in such a way that three types of interstitial site result. Today, the structure devised by Jamieson *et al.* is still accepted for SBN.

Recently, the development of integrated optical devices has stimulated the demand for thin films using attractive materials such as SBN. SBN thin films have been prepared by several techniques like sol-gel processing<sup>8</sup>, pulsed laser deposition<sup>9</sup> and metalorganic chemical vapor deposition (MOCVD)<sup>10</sup>. Recently, it has been proposed to prepare SBN thin films by a chemical method based on a polymeric resin containing metallic ions<sup>11</sup>.

In this work, SBN thin films were obtained by the above cited method. The effect of the temperature and crystal-

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Trabalho apresentado no 14º CBECIMAT, Águas de São Pedro, Dezembro 2000.

lization time on SBN thin films was studied using X-ray diffraction at room temperature. In addition, ferroelectric properties of films crystallized at fixed temperature but for different time duration were investigated.

## 2. Experimental

SBN films were prepared by a hybrid chemical method before mentioned. The general idea is to distribute the metallic ions homogeneously throughout the polymeric resin, prepared according to the Pechini method<sup>12,13</sup>. The process calls for forming a chelate between dissolved ions with a hydroxycarboxylic acid (citric acid). Heating of the resin in air causes a breakdown of the polymer. Subsequently, the ions are oxidized to form the desired crystalline phases.

Barium oxide (BaO), strontium carbonate (SrCO<sub>3</sub>) and ammoniac complex (NH<sub>4</sub>H<sub>2</sub>NbO(C<sub>2</sub>O<sub>4</sub>).3H<sub>2</sub>O) were selected as starting materials. The molar ratio of starting materials was calculated to obtain a final Sr<sub>0.75</sub>Ba<sub>0.25</sub>Nb<sub>2</sub>O<sub>6</sub> phase. For preparation of the resin, BaO, SrCO<sub>3</sub> and NH<sub>4</sub>H<sub>2</sub>NbO(C<sub>2</sub>O<sub>4</sub>).3H<sub>2</sub>O were initially dissolved separately in water or acid solution to form a transparent solution. Next, each solution was mixed separately with citric acid and heated to 40 °C for 30 min. Then, each solution was mixed with ethylene glycol (citric acid/ethylene glycol = 50/50) and polymerized by heating up to 100 °C for 30 min. Finally, the three solutions were mixed at room temperature, heated again to 50 °C and stirred for 20 min to homogenization, when a transparent final resin was obtained. The final resin used for deposition of films presented high stability. Previous stability investigation showed that these resins could be used after six months without appreciable changes in structural, microstructural and electric characteristics of the films.

Films of the resins were deposited at room temperature on Pt/Ti/SiO<sub>2</sub>/Si substrates by spin coating at 4500 rpm for 40 s. Films were obtained by depositing multiple layers of this resin. Each layer was annealed at 400 °C for 3 h, to remove the organic components. The process was repeated for eight deposited layers to obtain films with 0.5 μm thicknesses in average. For crystallization, films were annealed in electric furnace at 500 °C, 600 °C and 700 °C during one h. Additionally, extra film was crystallized at 700 °C for 5 h. The structure of the crystallized films at different time and firing temperatures was analyzed by X-ray diffraction (XRD) using CuK<sub>α</sub> radiation from a Rigaku rotating anode with an incident angle of 2°.

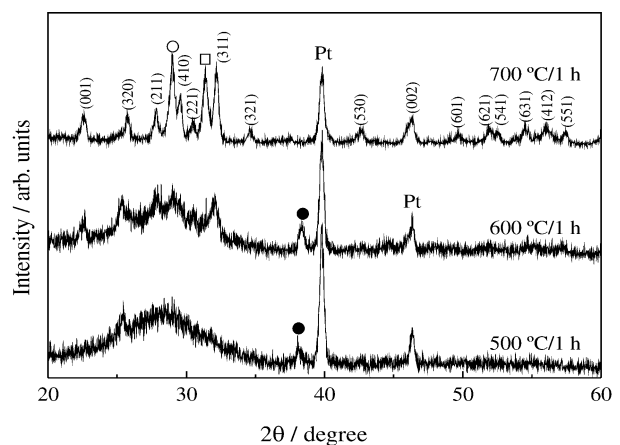
Ferroelectric properties were measured using Metal-Ferroelectric-Metal (MFM) capacitors. For this purpose, several electrodes of gold (0.5 mm in diameter) were deposited over an area of 1 x 1 cm<sup>2</sup> on the films through a mask to form MFM capacitors. P-E hysteresis loops obtained at a frequency of 100 Hz were measured using a

Sawyer-Tower circuit attached to a Tektronix 2232 digital oscilloscope. Scanning electron microscopy (SEM) was used to study the surface morphology of SBN films. Micrograph was made using a JEOL JSM-5800 microscope. All measurements were conducted at room temperature.

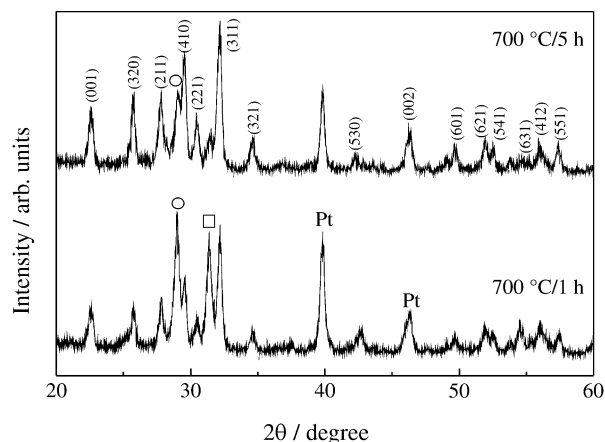
## 3. Results and Discussion

The effects of crystallization temperature in SBN films were studied. Fig. 1 shows XRD patterns of SBN thin films, heat-annealed at 500 °C, 600 °C and 700 °C for 1 h. Peaks identified in this figure were attributed to tetragonal SBN phase. Based on Fig. 1, it can be seen films crystallized at 700 °C presented better crystallization than films crystallized at 500 °C. This is confirmed by the better definition of XRD peaks for film crystallized at 700 °C. Considering XRD for films crystallized at 500 °C and 600 °C, the presence of the larger band for 2θ between 24° and 34°, characteristic of amorphous material, suggested that these films are only partially crystallized. The observed band may be associated with the presence of residual organics coming from decomposition of the polymeric resin or to bad crystallization of SBN films at low temperatures. For the film crystallized at 500 °C it can be seen a coexistence of amorphous phase and the initial crystallization of SBN phase, attested by the presence of the (320) reflection. When temperature increases from 500 °C to 700 °C, this band tends to disappear and the XRD background is smaller.

Figure 2 shows XRD patterns of SBN films crystallized at 700 °C for 1 h and 5 h. Some important features are observed in this figure. In both cases, it is possible to identify the presence of the SrNb<sub>2</sub>O<sub>6</sub> (SN) phase, XRD peak around 2θ = 29°, coexisting with SBN phase. SN is not a ferroelectric material with the tungsten bronze structure, which was formed with the ferroelectric SBN. When crystallization time increases from 1 h to 5 h, the intensity



**Figure 1.** X-ray diffraction patterns of SBN thin films deposited on Pt/Ti/SiO<sub>2</sub>/Si substrate. Films were crystallized at 500 °C, 600 °C and 700 °C (C) for 1 h. In this figure SrNb<sub>2</sub>O<sub>6</sub> (O), TiO<sub>2</sub> (□) and metallic Ti (●).



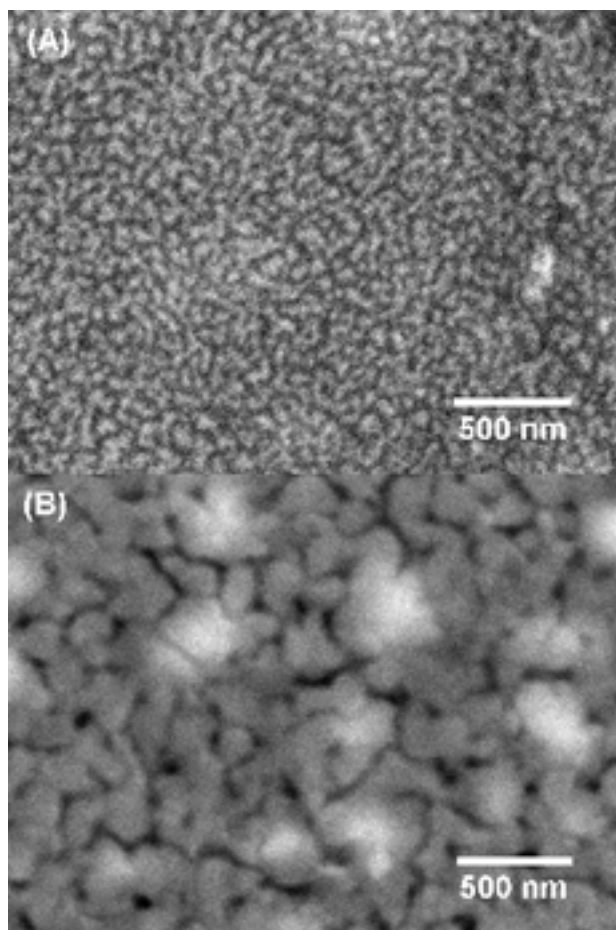
**Figure 2.** X-ray diffraction patterns of SBN thin films crystallized at 700 °C for 1 h and 5 h. In this figure SrNb<sub>2</sub>O<sub>6</sub> (O), TiO<sub>2</sub> (□) and metallic Ti (●).

of SN peak decreases. However, decrease in SN peak was accompanied by increases in (311) peak of SBN.

For samples prepared around  $x = 0.75$  ratio any compositional fluctuations or temperature and time of crystallization may favor the formation of SBN and SN together in same system<sup>14</sup>.

For SBN films crystallized at 700 °C for 1 and 5 h the lattice constants  $a$  and  $c$  were calculated for a tetragonal symmetry using ten of the most intense peaks of XRD patterns. For film crystallized for 1 h the values obtained of lattice constants  $a$  and  $c$  were 12.457 and 3.919 Å, respectively. These values were respectively 12.453 and 3.928 Å, for film crystallized for 5 h. These results were summarized in Table 1. The lattice parameters  $a$  and  $c$  obtained here agreed relatively well with results of the literature for SBN thin film, with same composition, obtained by metal-organic chemical vapor deposition (MOCVD), whose values are around  $a = 12.430$  Å and  $c = 3.932$  Å. For bulk crystals with same composition the lattice parameters are  $a = 12.458$  Å and  $c = 3.928$  Å<sup>15</sup>.

Crystallized films were crack-free, uniform and adhered well on substrates. Figure 3 shows the surface morphology of SBN film, crystallized at 700 °C for 1 h (Fig. 3-A) and at 700 °C for 5 h (Fig. 3-B). It can be seen that the film exhibits a dense microstructure. Thickness of the film was about 500 nm. In average, the grain sizes of the films were estimated to be around 80 nm, for film crystallized for 1 h, and around 200 nm, for film crystallized for 5 h. The average grain size of film crystallized for 5 h is almost two times greater than those of films crystallized for 1 h.



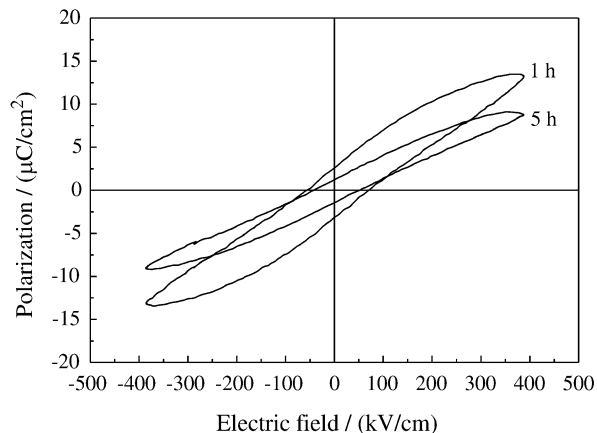
**Figure 3.** Scanning Electron Microscopy of the SBN thin film crystallized at 700 °C for 1 h (A) and at 700 °C for 5 h (B).

Ferroelectric characterizations were performed in films crystallized at 700 °C for 1 and 5 h. Figure 4 shows the P-E hysteresis loops obtained from these films. Based on Fig. 4, for the SBN film crystallized at 700 °C for 1 h, the obtained remanent polarization ( $P_r$ ) and the coercive field ( $E_c$ ) were 2.6  $\mu\text{C}/\text{cm}^2$  and 71.9 kV/cm, respectively. For film crystallized at 700 °C for 5 h these parameters were  $P_r = 1.1$   $\mu\text{C}/\text{cm}^2$  and  $E_c = 50.5$  kV/cm. As observed by XRD analysis, the SBN/SN ratio is greater in film crystallized for 5 h than film crystallized for 1 h. Thus, the observed difference in  $P_r$  probably reflects the kinetic of SBN film crystallization.

In the literature, reported values of  $P_r$  for SBN 75/25 films are around to 0.6  $\mu\text{C}/\text{cm}^2$  at room temperature<sup>16</sup>. However, the value of  $P_r$  increases up to 4.6  $\mu\text{C}/\text{cm}^2$  when

**Table 1.** Structural and ferroelectric characteristics for SBN films crystallized at 700 °C for 1 h and 5 h.

Crystallization time	$a$ (Å)	$c$ (Å)	$P_r$ ( $\mu\text{C}/\text{cm}^2$ )	$E_c$ (kV/cm)
1 h	12.457	3.919	2.6	71.9
5 h	12.453	3.928	1.1	50.5



**Figure 4.** Hysteresis loop, measured at 100 Hz, of SBN film crystallized at 700 °C for 1 h and 5 h.

measured at temperatures below 0 °C. This dependence reflect the fact that compositions near to 25 mol% of barium ( $x = 0.25$ ) presents a Curie temperature ( $T_c$ ) at room temperature around 50-54 °C<sup>15</sup>. Consequently, any compositional nonuniformity results in a phase transition located below the usual 50-54 °C transition temperature for SBN 75/25 films<sup>16</sup>.

#### 4. Conclusion

Polycrystalline SBN thin films were crystallized at different temperatures and time duration. Results showed good crystallization of SBN tetragonal phase when treated at 700 °C for 1 and 5 h. Undesired  $\text{SrNb}_2\text{O}_6$  (SN) phase appear mainly in films crystallized at 700 °C for 1 h. The amount of the SN phase decreases with increasing crystallization time. The observed smaller in remanent polarization for films crystallized for 5 h, in comparison with the film crystallized for 1 h, is probably related to the compositional fluctuation due to the SN formation.

#### Acknowledgements

The authors are grateful to CNPq and FAPESP (Process 99/02485-2) for financial support, to Dr. Yvonne P. Mas-

carenhas (IFSC-USP) for XRD facilities and to Mr. Francisco J. Picon (DF-UFSCar) for technical support.

#### References

1. Magneli, A. *Ark. Kemi*, v. 1, p. 213, 1949.
2. Glass, A.M. *J. Appl. Phys.*, v. 40, p. 4699-4713, 1969.
3. Zook, J.D.; Liu, S.T. *J. Appl. Phys.*, v. 49, p. 4604-4606, 1978.
4. Sakamoto, S.; Yazaki, T. *Appl. Phys. Lett.*, v. 22, p. 429-431, 1973.
5. Horowitz, M.; Bekker, A.; Fischer, B. *Appl. Phys. Lett.*, v. 62, p. 2619-2621, 1993.
6. Nishiwaki, S.; Takahashi, J.; Kodaira, K.; Kishi M. *Jpn. J. Appl. Phys.*, v. 35, p. 5137-5140, 1996.
7. Jamieson, P.B.; Abrahams, S.C.; Bernstein, J.L. *J. Chem. Phys.*, v. 48, p. 5048-5057, 1968.
8. Xu, Y.; Chen, C.J.; Xu, R.; Mackenzie, J.D. *Phys. Review B*, v. 44, p. 35-41, 1991.
9. Thöny, S.S.; Youden, K.E.; Harris Jr., J.S.; Hesselink, L. *Appl. Phys. Lett.*, v. 65, p. 2018-2020, 1994.
10. Lee, M.; Feigelson, R.S. *J. Crystal Growth*, v. 180, p. 220-228, 1997.
11. Mendes, R.G.; Araújo, E.B.; Klein, H.; Eiras, J.A. *J. Materials Sc. Letters*, v. 18, p. 1941-1943, 1999.
12. Pechini, M. *U.S. Pat. N° 3 330 697*, July 11, 1967.
13. Lessing, P.A. *Ceramic Bulletin*, v. 68, p. 1002-1007, 1989.
14. Xu Y. *Ferroelectric materials and their applications*, North-Holland, Amsterdam, p. 255, 1991.
15. Neurgaonkar, R.R.; Hall, W.F.; Oliver, J.R.; Ho, W.W.; Cory, W.K. *Ferroelectrics*, v. 87, p. 167-179, 1988.
16. Neurgaonkar, R.R.; Santha, I.S.; Oliver, J.R. *Mat. Res. Bull.*, v. 2, p. 983-988, 1991.

FAPESP helped in meeting the publication costs of this article