

# Structural and electrical properties of strontium barium niobate thin films crystallized by conventional furnace and rapid-thermal annealing process

R.G. Mendes

*Universidade Federal de São Carlos, Departamento de Física, Grupo de Cerâmicas Ferroelétricas, Caixa Postal 676, 13565-670 São Carlos, SP, Brazil*

E.B. Araújo<sup>a)</sup>

*Universidade Estadual Paulista, Departamento de Física e Química, Grupo de Vidros e Cerâmicas, Caixa Postal 31, 15385-000 Ilha Solteira, SP, Brazil*

J.A. Eiras

*Universidade Federal de São Carlos, Departamento de Física, Grupo de Cerâmicas Ferroelétricas, Caixa Postal 676, 13565-670 São Carlos, SP, Brazil*

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Strontium barium niobate (SBN) thin films were crystallized by conventional electric furnace annealing and by rapid-thermal annealing (RTA) at different temperatures. The average grain size of films was 70 nm and thickness around 500 nm. Using x-ray diffraction, we identified the presence of polycrystalline SBN phase for films annealed from 500 to 700 °C in both cases. Phases such as  $\text{SrNb}_2\text{O}_6$  and  $\text{BaNb}_2\text{O}_6$  were predominantly crystallized in films annealed at 500 °C, disappearing at higher temperatures. Dielectric and ferroelectric parameters obtained from films crystallized by conventional furnace and RTA presented essentially the same values.

## I. INTRODUCTION

The tungsten bronze family is one of several ferroelectric materials. Since 1949, when the tungsten bronze structure was deduced by Magneli,<sup>1</sup> numerous tungsten bronzes have been synthesized. The tungsten bronze family includes niobates such as  $(\text{Sr},\text{Ba})\text{Nb}_2\text{O}_6$  (SBN),  $(\text{Pb},\text{Ba})\text{Nb}_2\text{O}_6$  (PBN), and  $(\text{Pb},\text{K})\text{Nb}_2\text{O}_6$  (PKN). PBN and PKN are orthorhombic tungsten bronze structure with a point group  $mm2$ . On the other hand, SBN ( $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ ), with  $0.25 < x < 0.75$ , presents a tetragonal ( $4mm$ ) phase at room temperature. A solid solution of SBN exists in the binary  $\text{SrNb}_2\text{O}_6$ – $\text{BaNb}_2\text{O}_6$  system. Investigations using x-ray diffraction (XRD) suggested a morphotropic phase boundary around  $x = 0.25$ , which is characterized by the coexistence of the tetragonal and orthorhombic phases.<sup>2</sup>

The excellent ferroelectric and electro-optic properties exhibited by SBN make this material promising for a variety of applications. SBN has received great attention as a ferroelectric material due to its large pyroelectric coefficient,<sup>3</sup> piezoelectric,<sup>4</sup> and electro-optic properties.<sup>5</sup>

In recent years, 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>6</sup> pulsed laser deposition,<sup>7</sup> and metalorganic chemical vapor deposition (MOCVD).<sup>8</sup> Large-scale processing of high-quality thin films requires low-temperature synthesis, high reproducibility, simplicity in all processing steps, and low cost. Due to this fact, the search for new routes for film preparation remains an interesting and open subject in order to improve the stability of complex solutions, the control of the stoichiometry of the film composition, or to reduce the cost of the process. Very recently, the preparation of SBN thin films by a chemical method based on a polymeric resin containing metallic ions was proposed.<sup>9</sup> The method was successfully applied to prepare SBN thin films of good quality and homogeneity.

In this work, SBN thin films obtained by the early cited method were studied under its structural, dielectric, and ferroelectric properties. The effect of the different heat treatments on SBN thin films, using conventional furnace and rapid-thermal annealing (RTA), was studied. Dielectric and ferroelectric properties are presented for films crystallized at different temperatures.

<sup>a)</sup>Address all correspondence to this author.  
e-mail: eudes@fqm.feis.unesp.br

## II. EXPERIMENTAL PROCEDURE

In this work SBN films were prepared by a hybrid chemical method used to produce a polymeric resin.<sup>9</sup> The general idea is to distribute the metallic ions homogeneously throughout the polymeric resin, prepared according to the Pechini method.<sup>10</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 ( $\text{SrCO}_3$ ), and ammoniac complex  $[\text{NH}_4\text{H}_2\text{NbO}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}]$  were selected as starting materials. The molar ratio of starting materials was calculated to obtain a final  $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$  (SBN 75/25) composition. For preparation of the resin, BaO,  $\text{SrCO}_3$ , and  $[\text{NH}_4\text{H}_2\text{NbO}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}]$  were initially dissolved in water to form a transparent solution. Next, each solution was mixed separately with citric acid and heated to 40 °C for 30 min. This stage is important to form chelate between mixed cations with a hydroxycarboxylic acid (citric acid). 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 and heated again to 50 °C and stirred during 20 min to homogenization, when a transparent resin was obtained. The final transparent resin indicates that all metallic ions were distributed throughout the polymeric resin.

Films of the resins were deposited at room temperature on Pt/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 organic material. The process was repeated for eight deposited layers to obtain a dense film. Deposited films were crack free, uniform, and well adhered on substrates. For crystallization, films deposited on Pt/Si substrates were annealed in a conventional electric furnace at 500, 600, and 700 °C for 1 h. The rapid-thermal crystallization was carried out in a Research INC power controller Model 664F RTA furnace at 500, 600, and 700 °C for 60 s. This RTA process permits heating rates between 10 to 50 °C/s.

The structure of the crystallized films at different temperatures was analyzed by XRD using  $\text{Cu K}_\alpha$  radiation at room temperature. The morphological examination of SBN films was performed on a JEOL JSM-5800 (Tokyo, Japan) scanning electron microscope (SEM). The dielectric constant ( $\epsilon$ ) and dissipation factor ( $\tan \delta$ ) were measured from 500- to 500-kHz frequency using an HP 4194A impedance analyzer. A Sawyer-Tower circuit was used to measure the ferroelectric properties at 100 Hz.

## III. RESULTS AND DISCUSSION

SBN films of good quality were obtained in this work. Figure 1 shows an SEM photomicrograph of the cross-sectional view of SBN thin film deposited on Pt/Si substrate. This film was crystallized at 700 °C for 1 h using a conventional furnace. Based on Fig. 1, measured thickness of the film was 500 nm and grain size was around 70 nm, on average.

The effect of temperature crystallization in SBN films was investigated under different conditions. Figure 2 shows XRD patterns for SBN films crystallized by conventional furnace and RTA process. Peaks identified in this figure were attributed to tetragonal SBN phase. As shown in Fig. 2, polycrystalline SBN phase crystallizes better on films annealed at 600 and 700 °C for 1 h. Some structural fluctuation can be seen for films annealed at 500 °C [Fig. 2(A)] when the well-defined (211) and (400) peaks were observed. These peaks disappear for films crystallized at 600 °C [Fig. 2(B)] and 700 °C [Fig. 2(C)].

Based on XRD patterns, changes of full width at half-maximum (FWHM) for some (*hkl*) peaks represent the degree of crystallization as a function of annealing temperature. The FWHMs of (311) peak in Fig. 2 were 0.72°, 0.63°, and 0.57° for films respectively annealed at 500, 600, and 700 °C for 1 h. These facts show that when annealing temperature increases the crystallization of SBN films on Pt/Si is improved. In Fig. 2(A) we can also identify the presence of the  $\text{SrNb}_2\text{O}_6$  (SN) and  $\text{BaNb}_2\text{O}_6$  (BN) phases for films annealed at 500 °C for 1 h. When temperature increases, BN disappears but SN remains at film annealed at 600 and 700 °C for 1 h. Neither SN nor BN is a ferroelectric material with the tungsten bronze structure. They are components of the solid solution that yields ferroelectric SBN.

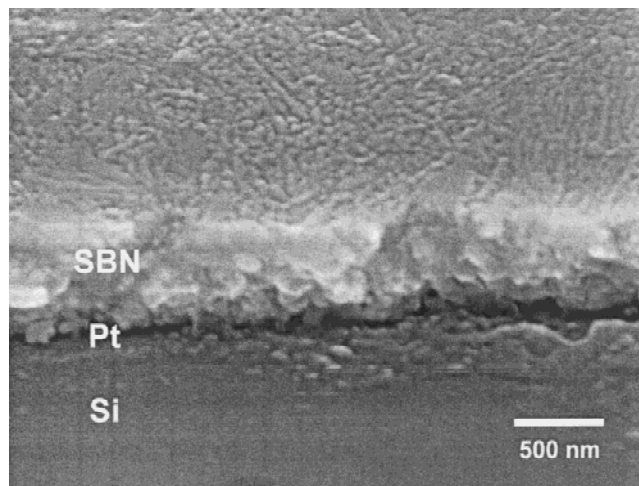


FIG. 1. Cross section of SBN thin film deposited on Pt/Si substrate and crystallized by a conventional furnace at 700 °C for 1 h.

Figure 2(D) shows XRD patterns of the SBN films crystallized by RTA at 700 °C for 60 s. The FWHM of the (311) peak was 0.57°, indicating similar behavior of SBN film crystallized by conventional method at same temperature. As observed in Fig. 2(D), SBN was crystallized without SN phase and this may be attributed to effective crystallization of the SBN phase using the RTA process. Films were also crystallized at 500 and 600 °C for 60 s using RTA, not shown here. These films presented essentially the same results, in terms of crystallization, as films crystallized in a conventional furnace at the same temperatures.

Based on XRD patterns of SBN films crystallized at 700 °C by conventional and RTA methods, the lattice constants  $a$  and  $c$  were calculated for tetragonal phase using the (001), (311), (002), and (322) peaks. For the film annealed by the conventional method, the calculated lattice constants were  $a = 11.57$  Å and  $c = 4.00$  Å, while  $a = 11.62$  Å and  $c = 4.03$  Å for film crystallized by RTA. The lattice parameters  $a$  and  $c$  obtained here

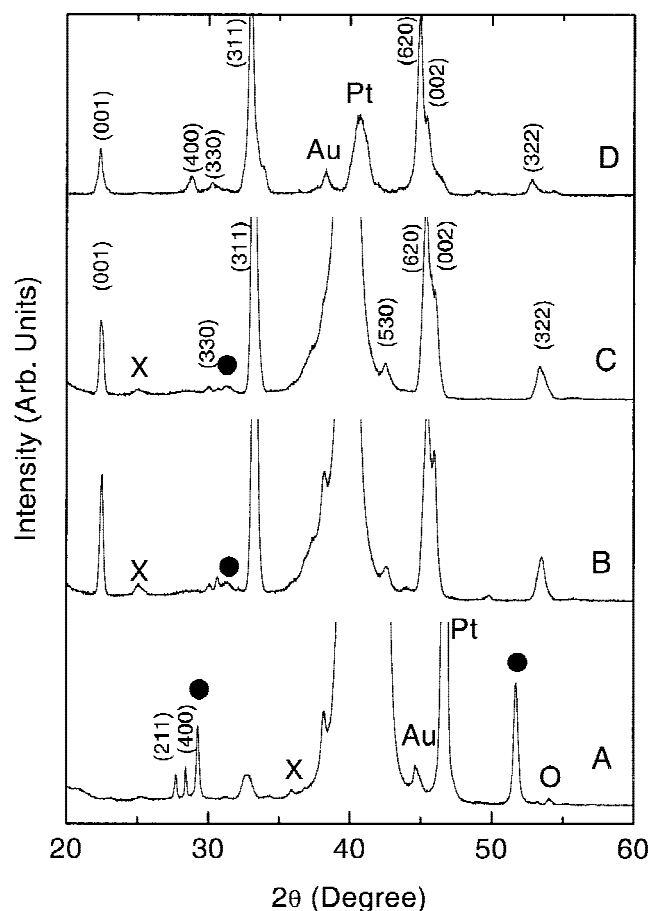


FIG. 2. XRD patterns of SBN thin films deposited on Pt/Si substrate. Films were crystallized by conventional furnace at (A) 500 °C, (B) 600 °C, and (C) 700 °C for 1 h and (D) by RTA process at 700 °C for 60 s. Symbols represent (x) unidentified phase, (●)  $\text{SrNb}_2\text{O}_6$ , and (○)  $\text{BaNb}_2\text{O}_6$ .

agreed relatively well with results of the literature for SBN 75/25 thin film obtained by MOCVD, whose values are around  $a = 12.430$  Å and  $c = 3.932$  Å.<sup>8</sup> For bulk crystals with the same composition the lattice parameters are  $a = 12.458$  Å and  $c = 3.928$  Å.<sup>11</sup>

Films annealed at 700 °C by the conventional method (for 1 h) and RTA (for 60 s) were used for dielectric and ferroelectric measurements because these films presented better crystallization. The dielectric behavior of the SBN films, examined in terms of the dielectric constant ( $\epsilon$ ) dissipation factor ( $\tan \delta$ ) as functions of measuring frequency, are summarized in Fig. 3.

It may be seen that dielectric constant exhibits a slight frequency dependency, which is consistent with the expected normal behavior. The dielectric constant and dissipation factor at a frequency of 100 kHz were 119 and 0.164, respectively, for film crystallized by the conventional method at 700 °C for 1 h. For film crystallized using the RTA method these values were respectively 107 and 0.088. The value of the dielectric constant obtained here is consistent with other reports for SBN thin films obtained through metal alkoxide.<sup>12</sup> The observed frequency dispersion at lower frequencies of the dissipation factor ( $\tan \delta$ ) is probably related to interfacial effects, often denominated the Maxwell–Wagner type.

Hysteresis loops were observed at room temperature, at 100 Hz. Figure 4 shows P-E hysteresis loop of SBN films crystallized by conventional furnace at 700 °C for 1 h and by RTA at 700 °C for 60 s. Rounded curves were found due to the low-frequency high-loss characteristics of the films. The remanent polarization ( $P_r$ ) and the coercive field ( $E_c$ ) were 17.8  $\mu\text{C}/\text{cm}^2$  and 180 kV/cm, respectively, for the SBN film annealed in a conventional furnace at 700 °C for 1 h. Similar results were obtained for films crystallized by the RTA method. This film presented  $P_r = 16$   $\mu\text{C}/\text{cm}^2$  and  $E_c = 155$  kV/cm. In the literature, reported values of  $P_r$  and  $E_c$  for SBN 75/25 films ranged from 1.9 to 34  $\mu\text{C}/\text{cm}^2$  and 51 to 180 kV/cm,

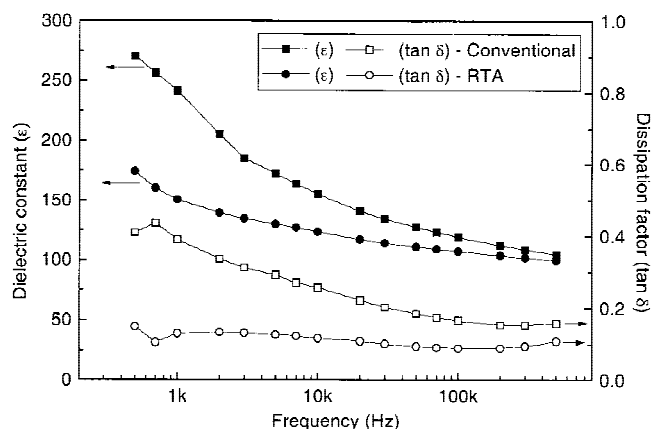


FIG. 3. Dielectric constant and dissipation factor for SBN thin films crystallized by conventional and RTA methods.

respectively, obtained by sol-gel.<sup>12,13</sup> In this work, the observed  $P_r$  is lower if compared with values observed for crystals, whose values ranged from 27 to 32  $\mu\text{C}/\text{cm}^2$ .<sup>11</sup> However, the coercive field ( $E_c$ ) and remanent polarization ( $P_r$ ) values obtained here for SBN thin films may not correspond to intrinsic values because the conductivity effect was not discounted in loop hysteresis of Fig. 4. Thus, the distortion observed on hysteresis is probably associated with the effect of conductivity in SBN films, which may be attributed to the presence of undesirable coexistence of phases on films such as  $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$  (SBN 75/25) and  $\text{SrNb}_2\text{O}_6$  (SN).

The capacitance–voltage (C–V) characteristic was also studied on films crystallized at 700 °C. A small alternating-current signal of 10-mV amplitude and 100-kHz frequency was applied across the sample while the direct-current electric field was swept from positive

bias to negative bias and back again. Figure 5 shows the C–V characteristic of the film crystallized by the conventional furnace; film prepared by RTA presented a similar result. The two maximas, which are due to ferroelectric polarization reversals, associated with double coercive field ( $E_c$ ), are clearly seen in Fig. 5. Generally the coercive field determined by C–V measurements are somewhat smaller than  $E_c$  determined from the hysteresis loop measurements due to dependence of  $E_c$  on the applied voltage and frequency. Note that the two peaks are of different height and there is a small offset toward positive bias. Considering a ferroelectric, the polarization and dielectric constant vary nonlinearly with applied field. In some cases, a space charge is formed at interfaces and, under conditions of reverse bias, a depletion layer forms.<sup>14</sup> Asymmetry and shift in C–V curve may be observed if a disparity of the space charge occurs. In general, observed effects are associated with contacts and may be minimized with adequate postannealing of the films.

#### IV. CONCLUSIONS

Polycrystalline SBN thin films of high density were crystallized on Pt/Si substrates using a polymeric resin. Results showed good crystallization of SBN films, crystallized using a conventional furnace or RTA. Undesired phases such as  $\text{SrNb}_2\text{O}_6$  and  $\text{BaNb}_2\text{O}_6$  appear in films deposited at 500 °C but these phases disappear at higher temperatures. Finally, dielectric and ferroelectric parameters presented essentially the same values for films crystallized by a conventional furnace and RTA. Thus, for purposes of future applications in microelectronic devices, the preparation of SBN films by the RTA method is of interest. In this case, the final product will be less expensive than other SBN thin films produced by other physical methods. The main and distinct advantage over other chemical methods, especially sol-gel, is associated with the high stability observed in polymeric resin used on film deposition. Previous stability investigations showed that these resins could be used after 1 year without appreciable changes in structural, microstructural, and electric characteristics of the films. The next step is to study ideal conditions to eliminate or minimize undesirable observed effects in dielectric characteristics of the SBN films.

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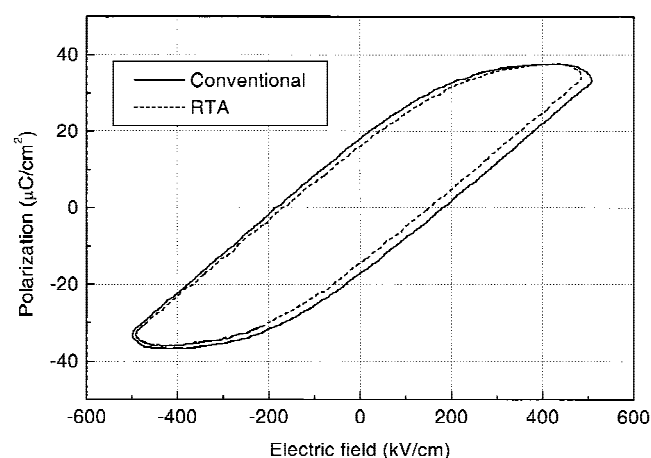


FIG. 4. Hysteresis loop, measured at 100 Hz, of SBN film annealed by a conventional furnace at 700 °C for 1 h and RTA at 700 °C for 60 s.

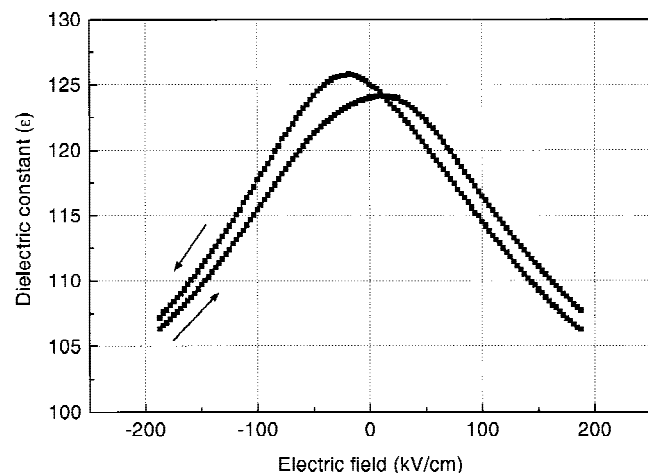


FIG. 5. C–V characteristic of SBN thin film crystallized by a conventional furnace at 700 °C for 1 h.



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