SYNTHESIS AND PROPERTIES OF FERROELECTRIC STRONTIUM BARIUM NIOBATE ($Sr_{0.75}Ba_{0.25}Nb_2O_6$) THIN FILMS

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ABSTRACT
Strontium barium niobate (SBN) belong to the class of ferroelectric materials that has an open tungsten bronze structure and presents high pyroelectric coefficient and excellent electro-optic properties. The integrated device technology point toward the use of thin films with excellent properties like SBN. In such way, this work, describe and characterize SBN thin films prepared by an alternative chemical method. The structural, dielectric and ferroelectric properties of the obtained thin films were investigated. The results pointed to high quality films with single polycrystalline SBN phase, dielectric constant around 600, low dielectric dissipation factor ($\tan\delta < 0.05$) and slim ferroelectric hysteresis loop behavior.

Key words: ferroelectric, thin film, strontium barium niobate.

RESUMEN
Materiales de niobato de estroncio y bario (SBN) pertenecen a la clase de ferroeléctricos, con estructura tipo tungsteno bronce abierta, que presentan elevados coeficientes piroeléctricos y excelentes propiedades electro-ópticas. La tecnología de los dispositivos integrados induce al uso de capas delgadas basadas en SBN debido a las excelentes propiedades que manifiesta. De esta manera, este trabajo describe y caracteriza capas delgadas de SBN preparadas por un método químico alternativo. Fueron investigadas las propiedades estructurales, dieléctricas y ferroeléctricas de las capas delgadas obtenidas. Los resultados mostraron capas de alta calidad, presentando una fase única policristalina de SBN de constante dieléctrica alrededor de 600, bajo factor de disipación dieléctrico ($\tan\delta < 0.05$) y lazos de histéresis cerrados.

Palabras clave: ferroeléctricos, capas delgadas, niobato de estroncio y bario

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 [1] deduced the tungsten bronze structure. The tungsten bronze family is one of several ferroelectric materials that includes niobates such as $(Sr,Ba)Nb_2O_6$ (SBN), $(Pb,Ba)Nb_2O_6$ (PBN) and $(Pb,K)Nb_2O_6$ (PKN). The PBN and PKN are orthorhombic tungsten bronze structure with a point group mm2. On the other hand, SBN ($Sr_xBa_{1-x}Nb_2O_6$), with $0.25 < x < 0.75$, presents a tetragonal (4 mm) structure at room temperature.

The SBN structure was studied by Jamieson **et al**. [2] using X-ray diffraction. This structure consists of a framework of NbO_6 octahedra sharing corners in such a way that three types of interstitial site result. The occupation of these sites can be changed with the SBN composition promoting great influences in SBN properties [3].

The high pyroelectric coefficient [3] and excellent electro-optic properties [4,5] make the SBN a very attractive material for applications that include pyroelectric detectors [6], optical waveguides [7] and holographic image storage devices [8].

Recently, the development of integrated devices has stimulated the demand for thin films of attractive materials such as SBN. SBN thin films have been prepared by several techniques like sol-gel processing [9], pulsed laser deposition [10] and metalorganic chemical vapor deposition (MOCVD) [11]. However, 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 thin film preparation remains as an interesting and open subject in order to improve the stability of complex solutions, to the control of thin film composition or to reduce the processing costs.

In this work, SBN thin films were obtained by an alternative chemical method based on the preparation and deposition of a resin containing the metallic formation ions of the desired phase incorporated in a

polymeric matrix. The structural, dielectric and ferroelectric properties of the obtained thin films were investigated.

EXPERIMENTAL PROCEDURE

The proposed chemical method for the preparation of the deposition resin is based in the Pechini method [12]. The general idea is to distribute the metallic ions homogeneously throughout a polymeric resin. The process calls for forming a chelate between dissolved ions with a hydroxycarboxylic acid. After the addiction of a poly hydroxyl alcohol and the increasing in the temperature up to 100 °C occur the solution polyesterification and the ions remain incorporated in the polymeric matrix.

For the SBN resin, strontium carbonate ($SrCO_3$), barium carbonate ($BaCO_3$) and ammoniacal complex $NH_4H_2[NbO(C_2O_4)_3].3H_2O$ were separately dissolved. Each of these ions dissolved solutions were mixed with citric acid and heated up to 40 °C to form the chelates. The chelate solution was mixed with ethylene glycol (citric acid/ethylene glycol = 50/50) and polymerized by heating up to 100 °C. Finally, the three solutions were mixed, stirred and heated up to 50 °C promoting the homogenization. The final transparent resin indicates that all metallic ions were distributed throughout the polymeric resin.

The molar ratio of the dissolved starting precursors ($SrCO_3$, $BaCO_3$ and ammoniacal complex) determines the composition of the thin films obtained with the final resin. Knowing the ions concentration of each individual resins, a desired thin film composition can be obtained by the simple proportional mix of the individuals resins. For this work, the molar ratio was calculated to the preparation of SBN thin films with the composition $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (SBN75/25).

Figure 1 resumes the main preparation steps of the polymeric SBN resin and of the thin films preparation and characterization.

The SBN thin films, with 500 nm in thickness, were prepared throughout the deposition (spin coating) of eight successive layers of the final resin on $Pt/Ti/SiO_2/Si$ substrates. Each layer was annealed at 400 °C for 3 hours, to remove the organic compounds. For crystallization, films were annealed in a conventional electric furnace at 700°C during one hour.

The structure of the crystallized films was analyzed by X-ray diffraction (XRD) using CuK_α radiation and 2^o of incident beam angle in a Rigaku Rotaflex RU200B equipment. The dielectric constant (ε) and dissipation factor (tanδ) at room temperature were measured from 1 kHz to 1 MHz frequency utilizing a HP4194A impedance analyzer. The ferroelectric properties were investigated at room temperature and 100 Hz frequency using a Sawyer-Tower circuit.

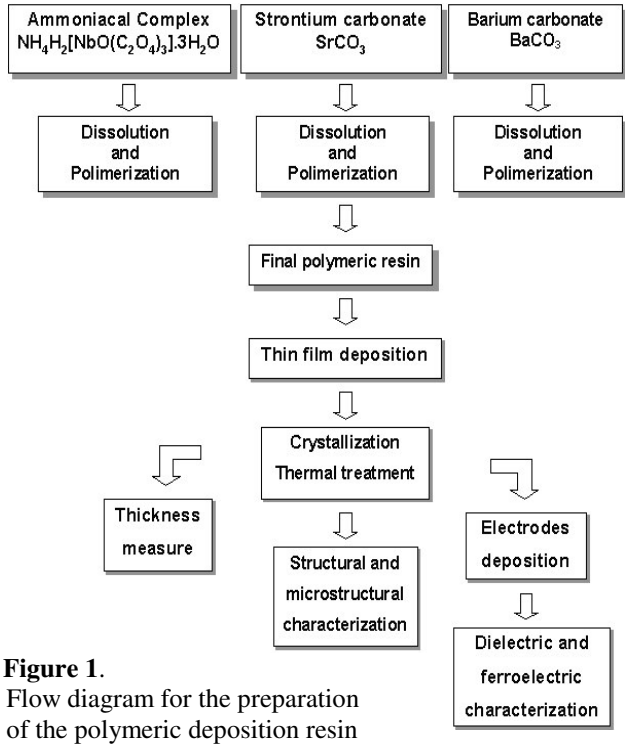

Figure 1.
Flow diagram for the preparation of the polymeric deposition resin and thin films preparation and characterizations.

RESULTS AND DISCUSSION

Compositional analyses realized in the obtained SBN thin films using Energy Dispersive Spectrometry (EDS) showed Sr/Ba and (Sr+Ba)/Nb ratios 3.2 and 0.48, respectively. These values are close to that expected for the SBN75/25 composition (Sr/Ba = 3.0 and (Sr+Ba)/Nb = 0.5). In such way, no significant compositional changes from the resin to the thin films were noted.

Figure 2 shows the XRD pattern for the SBN thin film crystallized at 700 °C for 1 hour. As can be seen, the XRD pattern shows only peaks of the platinum substrate layer and of the polycrystalline SBN tetragonal phase. In the X-ray detection range, the patterns do not show evidence of secondary phases.

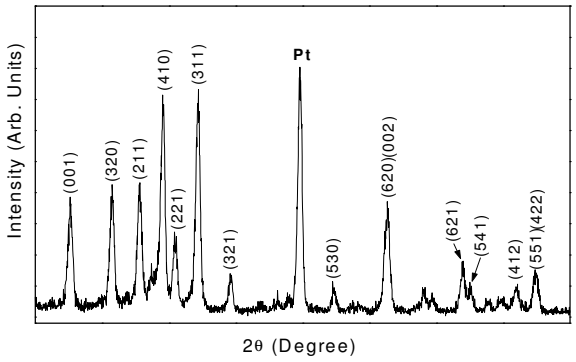

Figure 2. X-ray diffraction pattern for SBN thin film deposited on $Pt/Ti/SiO_2/Si$ substrate crystallized at 700°C for 1 hour.

Based in the high intensity peaks identified in the XRD pattern the tetragonal lattice constants a and c were calculated. The obtained parameters a = 12.442(5) Å and c = 3.925(5) Å were in relatively well agreement with literature results for SBN75/25 in single crystals form (a = 12.458 Å and c = 3.928 Å) [13] and oriented (00l) SBN thin films form (a = 12.456 Å and c = 3.912 Å) [14].

The differences from the film to the single crystal parameters can be attributed to the presence of residual stress in the films originated by the different film/substrate thermal expansion coefficients. For the thin films parameters comparison, we can assume that they are submitted to the same residual stress. In such way, we can observe that the volume cells are very similar 607.6 $Å^3$ and 606.9 $Å^3$ for our polycrystalline and for the Neurgaonkar [14] oriented thin films, respectively. Therefore, we can conclude that the occupations of the unit cells were the same and that the small differences can be result of the orientation in the SBN Neurgaonkar films.

The dielectric behavior examined in terms of the dielectric constant (ε) and dissipation factor (tan δ) as functions of the measuring frequency are showed in Figure 3.

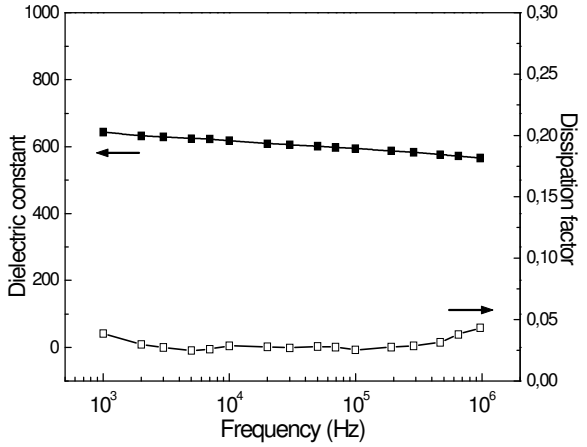

Figure 3. Dielectric constant and dissipation factor at room temperature as a function of the measuring frequency for SBN thin films.

It may be seen that the dissipation factor exhibit low values (tanδ < 0.05) and the dielectric constant do not present a high frequency dependency. The dielectric constant and dissipation factor for the typical 100 kHz frequency were 595 and 0.02, respectively.

The P-E hysteresis loop at room temperature and 100 Hz frequency is showed in Figure 4. As we can note, a slim hysteresis loop behavior was observed. The values of remanent polarization (P_r) and coercive field (E_c) were 0.5 μC/cm^2 and 12 kV/cm, respectively.

The Figure 4 inset shows dielectric measurements as a function of temperature realized in the thin films prepared in this work [15]. The characterization pointed to a ferroelectric-paraelectric phase transition near the room temperature. This result is in well agreement with literature results for SBN75/25 single crystals [3] and ceramics [16]. In this temperature region, the ferroelectric parameters tend to be reduced and slims hysteresis loops were really expected agreeing with the ferroelectric characterizations.

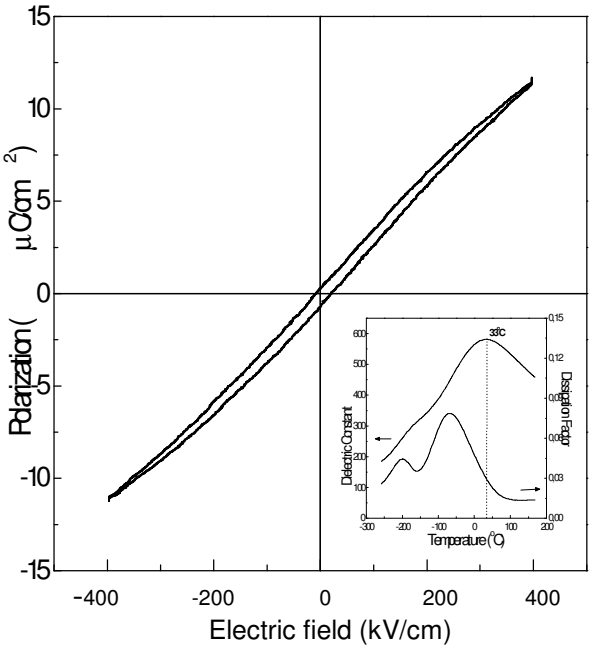

Figure 4. Hysteresis loop of SBN thin film, measured at 100 Hz frequency and room temperature. Inset: Dielectric constant and dissipation factor at 100 kHz frequency as a function of the temperature for the SBN thin films.

CONCLUSIONS

SBN thin films with the composition $Sr_{0.75}Ba_{0.25}Nb_2O_6$ were obtained by an alternative chemical method. The structural characterization showed a single poly-crystalline SBN phase with no evidence of secondary phases. The dielectric properties at room temperature pointed to a frequency independent dielectric constant values and reduced dissipation factors values attesting the good quality of the films. The ferroelectric characterization showed slim hysteresis loops, compatibles with the predicted Curie temperature for SBN with the same composition expected to the films.

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