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Influence of neodymium and lanthanum doping in the pyroelectric properties of strontium barium niobate (SBN) thin films

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Abstract

Strontium barium niobate thin films (SBN) are ferroelectric materials that can exhibit excellent pyroelectric and electro-optic properties. These properties make the SBN a very interesting material for a large variety of applications that include pyroelectric sensors. SBN thin films with a nominal composition $(Sr_{0.75}Ba_{0.25})Nb_2O_6$, known as SBN75/25, doped with lanthanum or neodymium (1.0, 1.5 and 2.0 mol%) were obtained by a chemical method, in order to investigate the influence of the doping on their pyroelectric responsivity. The pyroelectric response was obtained through voltage measurements in the films, caused by the incidence of a square laser pulse applied with a different repetition rate. Structural and dielectric characterizations revealed a single polycrystalline SBN phase and a decrease of the dielectric permittivity due to the doping. The experimental results show that the additions of the dopant elements increase the pyroelectric response of the films and decrease the frequency dependence of the pyroelectric voltage responsivity R_V, compared with the undoped one.
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Keywords: Ferroelectric; Pyroelectric; Strontium barium niobate; Thin films

1. Introduction

Strontium barium niobate ($Sr_xBa_{1-x}Nb_2O_6$- SBN) is a well known solid solution of strontium niobate ($SrNb_2O_6$) and barium niobate ($BaNb_2O_6$) in the range $0{,}25 < x < 0{,}75$. The excellent ferroelectric and electro-optic properties exhibited by SBN make this material promising for a variety of applications. These solid solutions present technological and academic importance due to the very good ferroelectric properties, photorefractive effect,[1] large pyroelectric[2] and piezoelectric[3] coefficients and electro-optic[4] properties.

It is well known that ferroelectric thin films for IR sensors present several advantages, compared with bulk materials. The advantages are the low heat capacity, possibility to make 2 D arrays and to be integrated more easily in electronic circuits. Therefore, the thin films properties optimization and the search for new compositions for application in such devices remains an interesting subject.

In this work, lanthanum or neodymium doped SBN thin films were obtained by a chemical method. In order to investigate their potential as infrared sensors, the influences of each doping element in the dielectric and pyroelectric properties were investigated.

2. Experimental procedure

The SBN films were prepared following a hybrid chemical method, used to produce a polymeric metallic ions resin.[5] The general idea is to distribute the metallic ions homogeneously throughout the polymeric resin, prepared according to the Pechini method.[6] Strontium carbonate ($SrCO_3$), barium carbonate ($BaCO_3$), ammoniac complex ($NH_4H_2NbO(C_2O_4).3H_2O$), neodymium oxide (Nd_2O_3) and lanthanum oxide (La_2O_3) were selected as starting materials. The molar ratio of starting materials was calculated to obtain a final $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (SBN75/25) composition containing 0,0; 1,0; 1,5 or 2,0 mol% of neodymium or lanthanum.

The films were obtained through the deposition of multiple resin layers on $Pt/Ti/SiO_2/Si$ substrates. Each

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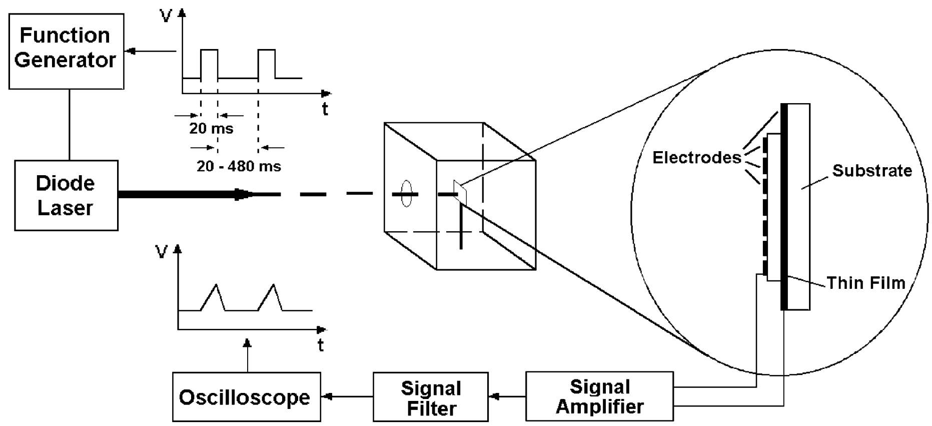

Fig. 1. Experimental setup for pyroelectric characterization.

layer was firstly annealed at 400 °C for 1 h to remove the organic compounds. The SBN polycrystalline phase was achieved after a crystallization thermal treatment at 700 °C for 1 h. The final film thickness was around 500 nm for eight layers.

Microstructure revealed using Atomic Force Microscopy—AFM (Digital Instruments—Nanoscope MultiMode IIIa) presented a dense microstructure and an average grain size of 65 nm. The structure of the crystallized films was analyzed at room temperature by X-ray diffraction (XRD) using CuK_α radiation in a Rigaku Rotaflex RU200B equipment

For dielectric and pyroelectric investigations thin (nearly transparent) gold electrodes (1.0 mm in diameter) were sputter deposited on the film surface forming a metal-film-metal configuration. Dielectric properties were investigated at room temperature as a function of the frequency (200 Hz–200 kHz) using an HP4194A Impedance Analyzer. Before the pyroelectric measurements the films were submitted to an external dC electric field. However, because the Curie temperature for the investigated compositions lies around 25–27 °C (near the measuring temperature), the films could not remain fully poled. The pyroelectric characterization was performed using a dynamic method, based on the measurements of the voltage in the samples, caused by small temperature changes induced by a laser modulated beam. A square modulated laser pulse of 160 mW, with 20 ms width and a repetition rate varying between 20 and 480 ms, was chopped in the individual electrodes. A schematic diagram of the pyroelectric measurement procedure is presented in Fig. 1.

3. Results and discussions

The X-ray diffraction patterns for SBN75/25 thin films doped with neodymium and lanthanum are showed in Fig. 2A and B, respectively. For the both cases only the presence of the tetragonal polycrystalline

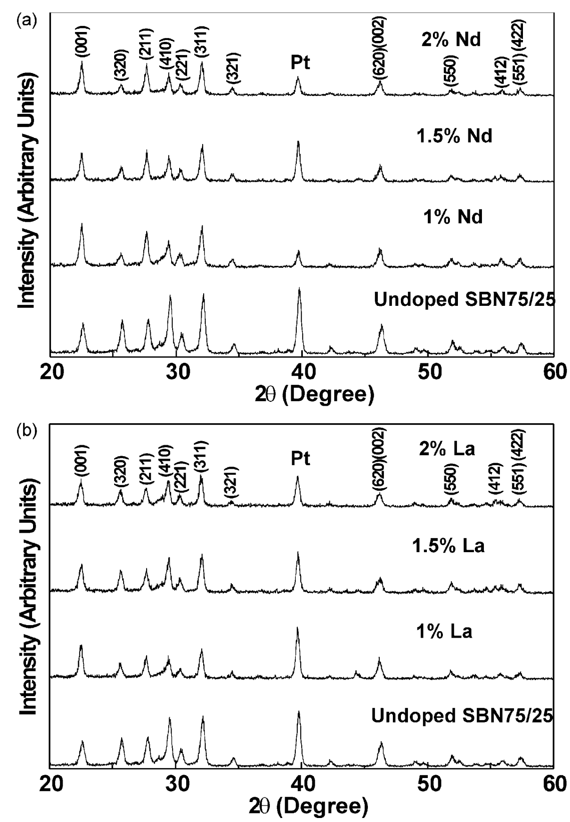

Fig. 2. X-ray diffraction patterns for the SBN75/25 thin films doped with (A) neodymium and (B) lanthanum.

SBN phase is observed, without any evidence of secondary phases or segregation of the dopant elements even for the highest concentration. This indicates total incorporation that the dopant in the SBN crystalline structure. For all the neodymium doped films, a small increase in the (211) relative peak intensity was observed. The occupation of the neodymium in the SBN unit cell can favor the (211) plane diffraction. Comparing the undoped films with lanthanum doped films no substantial changes in the relative peak intensity was noted.

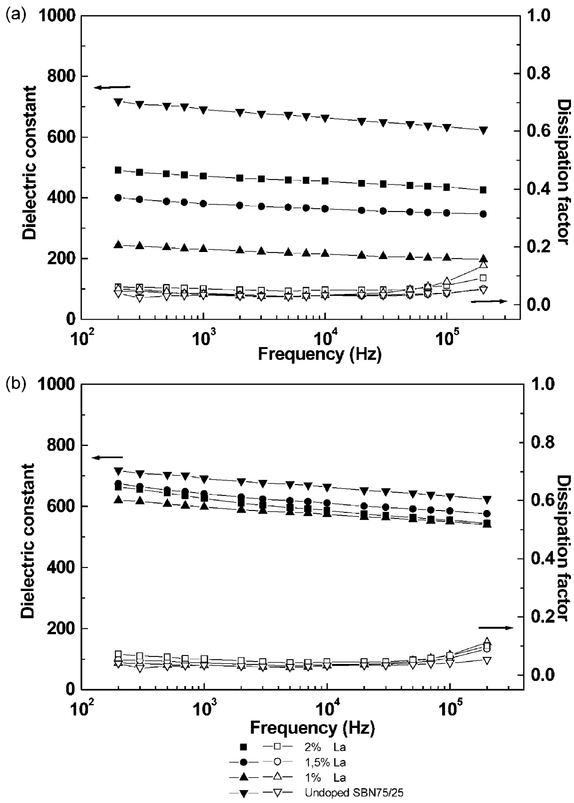

Fig. 3. Dielectric constant and dissipation factor as a function of frequency for the SBN75/25 thin films doped with (A) neodymium and (B) lanthanum.

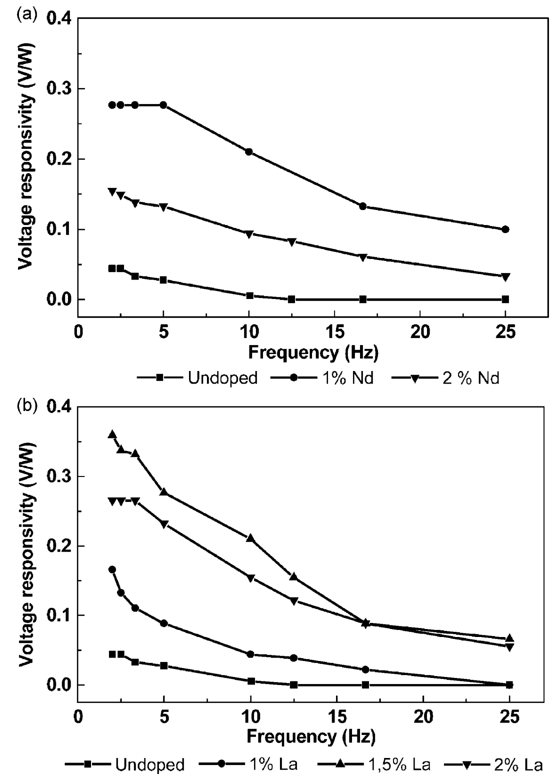

Fig. 4. Voltage responsivity as a function of the repetition frequency of the laser pulse for the SBN75/25 thin films doped with (A) neodymium and (B) lanthanum.

Fig. 3 presents the frequency dependence of dielectric permittivity (ϵ) and dissipation factor (tgδ) for the investigated SBN compositions doped with neodymium (Fig. 3A) and lanthanum (Fig. 3B). It can be seen a slight decrease of ϵ as the frequency is increased while tgδ remain almost frequency independent until 50 kHz for all investigated compositions. Above 50 kHz, the increase in the tgδ values can result of the electrode-film interfaces defects.[7] The dielectric permittivity of the doped films is lower than that of the undoped films, showing minimum values for a concentration of 1% of La or Nd and increasing for higher concentrations. A decrease in the dielectric permittivity is desired to improve the pyroelectric voltage figure-of-merit.[8] In this sense the films doped with 1% La or Nd should have the highest pyroelectric response.

The pyroelectric voltage responsivity is shown in Fig. 4 for undoped and neodymium (Fig. 4A) or lanthanum doped (Fig. 4B). The responsivity R_V was obtained dividing the voltage measured in each electrode by the laser power.[8,9] A higher responsivity can be observed for the doped films. It is not clear if is there a systematic change in the absolute responsivity with the amount of the dopant elements. The changes caused in the dielectric permittivity by the doping of SBN75/25 with La or Nd cannot alone explain such variations in

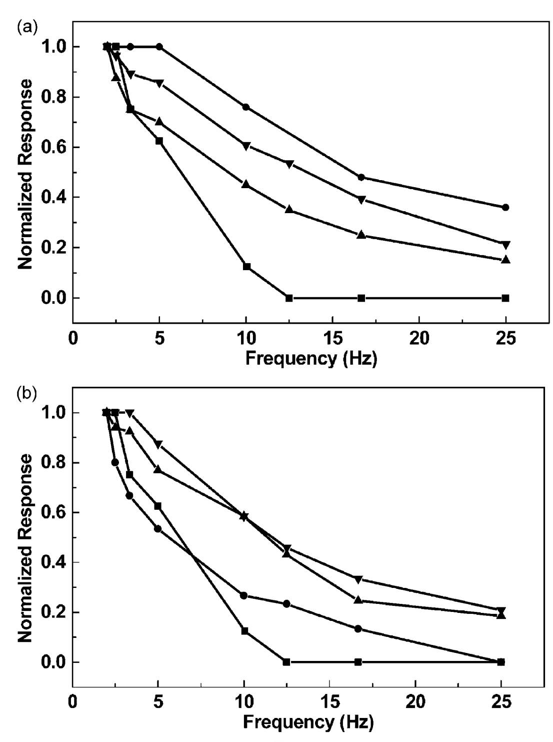

Fig. 5. Normalized voltage responsivity as a function of the repetition frequency of the laser pulse for the SBN75/25 thin films doped with (A) neodymium and (B) lanthanum.

the absolute responsivity. In our results the observed changes in the absolute responsivity values can be also influenced by a difference in the reflectivity of electrodes.

In order to compare the frequency dependence of the responsivity measured for each sample, the normalized responsivity [$R_N = RV(f) / R_V(2,5)$] is presented in Fig. 5. All investigated doped SBN present a lower frequency dependence of R_N, compared with the undoped SBN.

4. Conclusions

Strontium barium niobate SBN75/25 thin films doped with neodymium or lanthanum were prepared through a chemical method with a single polycrystalline SBN phase. Dielectric characterizations evidenced that the thin films presented low dissipation factors values and, in general, the dielectric constants for doped SBN are lower than those obtained for undoped films. The pyroelectric voltage responsivity of the doped films showed higher values than that obtained for undoped SBN. In the lanthanum doped SBN, the voltage responsivity increases with the increase of the lanthanum doping concentration. The frequency dependence of R_V is decreased by doping with La or Nd.

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