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# *Lead-free KNN-based thin films obtained by pulsed laser deposition*


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***Abstract*— In this work, $0.96(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}Nb_{0.94}Sb_{0.06}O_3$-$0.04Ba_{0.94}Ca_{0.06}ZrO_3$ (KNLNS-BCZ) and $0.98(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}Nb_{0.95}Sb_{0.05}O_3$-$0.02Ba_{0.5}(Bi_{0.5}Na_{0.5})_{0.5}ZrO_3$ (KNLNS-BBNZ) ferroelectric thin films were obtained by pulsed laser deposition. The structural, and morphological characteristics were studied to determine the best deposition parameters and analyse the piezoelectric properties. The studied deposition parameters were temperature, laser fluence, oxygen partial pressure and frequency. These parameters impact important characteristics of the thin films like grain morphology, thickness, and roughness. KNLNS-BCZ thin films with pure perovskite structure, homogeneous grain growth, and thickness ≥100 nm were fabricated at 700 °C, 2 J/cm$^2$, 300 mTorr, and frequencies of 5 Hz and 10 Hz. These films presented good ferroelectric behaviour and piezoelectric coefficient $d_{33eff}$ of 83.80 pm/V and 25.80 pm/V, respectively.**



***Keywords—Lead-free thin films, PLD method, and KNN-based.***


## I. INTRODUCTION

Piezoelectric thin films are employed in different technological applications such as actuators, sensors, micromechanical systems, and energy harvesters. Fabrication of materials as thin films allows their integration into several types of devices as microelectromechanical systems (MEMS). The properties of thin films and their fabrications cost differ significantly depending on the deposition method, which are divided in chemical and physical. Pulsed laser deposition (PLD) and sputtering are widely used as physical methods for thin film fabrication. PLD method has been employed to fabricate thin films from materials with complex compositions, which avoids the solubility issues related to chemical solution deposition methods. (K,Na)NbO3 (KNN) ferroelectric ceramic is one of the most promising lead-free materials due to its high Curie temperature and relatively high piezoelectric properties [1]. However, the volatilization of alkali metals in both bulk and thin films has been a challenge to develop materials for electronic applications. One option to avoid volatilization is doping the material with some cation, mainly lithium antimonate [2], which can also increase the density and helps to improve the piezoelectric properties. KNN-based thin films have been obtained by different routes: a) Chemical deposition as spin coating and spray coating of a precursor solution [3–5], or b) Physical deposition by sputtering or laser ablation. Among them, laser ablation, also called pulsed laser deposition (PLD), allows to obtain KNN thin films doped with different compounds as $BaZrO_3$, $LiSbO_3$, $(Bi,Na)TiO_3$, etc [6–8]. The main deposit parameters to consider are laser wavelengths, power density, repetition rate, substrate temperature, background pressure and gas atmosphere. Then, in this work the deposition parameters of two KNN-based thin films composition, $0.96(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}Nb_{0.94}Sb_{0.06}O_3$-$0.04Ba_{0.94}Ca_{0.06}ZrO_3$ and $0.98(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}Nb_{0.95}Sb_{0.05}O_3$-$0.02Ba_{0.5}(Bi_{0.5}Na_{0.5})_{0.5}ZrO_3$ obtained by PLD were studied. The structural, microstructural, and piezoelectric properties of the films were analysed.

## II. EXPERIMENTAL PROCEDURE

### *A. Thin films fabrication*

Ceramic targets of KNLNS-BCZ and KNLNS-BBNZ of 20 mm in diameter were prepared by conventional solid-state method. Detailed procedure and more information regarding the target's preparation of KNLNS-BCZ and KNLNS-BBNZ are reported elsewhere [9, 10]. Thin films of KNLNS-BCZ and KNLNS-BBNZ were deposited on $Pt/TiO_2/SiO_2/Si$ substrates by pulsed laser deposition (PLD) using a KrF Excimer laser (λ=248 nm). The films were obtained under different conditions of temperature, laser fluence, oxygen partial pressure ($PO_2$) and frequency (Table 1).

**Table 1**. Parameters used for the KNLNS-BCZ and KNLNS-BBNZ thin films deposition for different tests

| Parameter | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Temperature (°C) | 700, 725, 750 and 800 | 700 | 700 | 700 |
| Fluence (J/cm$^2$) | 2.5 | 2.5, 2.0, 1.5 | 2.0 | 2.0 |
| $PO_2$ (mTorr) | 100 | 100 | 100, 200, and 300 | 300 |
| Frequency (Hz) | 10 | 10 | 10 | 10 and 5 |

### *B. Thin films characterization*

The structure of KNLNS-BCZ and KNLNS-BBNZ thin films were identified by X-Ray Diffraction (XRD) technique (Rigaku, Ultimate IV). The grain morphology and thickness were observed by scanning electron microscopy (SEM) (JEOL JSM-6400). The grain size and thickness were determined by the ImageJ software. The piezoelectric properties of the thin films with good structural and microstructural properties were determined by Piezoresponse Force Microscopy (Park Systems Launch XE7).

## III. Result and discussion

### A. Structural characteristics

The temperature used during the deposition has an important impact in the crystallinity of the thin films. Fig. 1a-1b show the XRD patters of KNLNS-BBNZ and KNLNS-BCZ thin films deposited at 100 mTorr, 2.5 J/cm$^2$ and 10 Hz, at 700, 725, 750 and 800 °C. In both compositions, the patterns show a perovskite structure with secondary phases in most of the films. Previous reports have described the secondary phases due to the alkali metals volatility, forming pyrochlore or ternary oxide with different stochiometric instead of perovskite structure [11, 12]. The XRD patterns suggests that the thin films obtained at 700 °C have a smaller secondary phase. Fig. 1c-1d show the laser fluence effect on structural characteristics of KNLNS-BBNZ and KNLNS-BCZ samples obtained at 100 mTorr, 700 °C and 10 Hz. The thin films obtained at 2.5, 2.0 and 1.5 J/cm$^2$ fluence present a perovskite structure and secondary phase, which diminished as the fluence decreased. Moreover, the KNLNS-BCZ films show less secondary phase compared with KNLNS-BBNZ samples at low fluence. Nevertheless, both compositions were obtained with fewer impurities at 2.0 J/cm$^2$ compared to the previous step. Then, the fluence was set at this value. The oxygen partial pressure helps to avoid oxygen vacancies, obtaining thin films with minimal leaking. Fig. 1e-1f present the influence of the $PO_2$ variation on XRD patterns of KNLNS-BBNZ and KNLNS-BCZ thin films obtained at 2 J/cm$^2$, 700 °C, and 10 Hz. The patters show a remarkable improvement in the structural characteristics, decreasing the amount of secondary phase as the $PO_2$ increases. The purer films are observed at higher $PO_2$ as a result of the decrease in the volatilization of light cations due to the oxygen-rich environment inside the chamber. The frequency of the pulsed laser is associated with the material deposited speed on the substrate controlling the thickness and the final morphology.

Fig. 1g-1h show the XRD pattern of the KNLNS-BBNZ and KNLNS-BCZ thin films fabricated at 300 mTorr, 2 J/cm$^2$, 700 °C, and frequencies of 5 and 10 Hz. The patterns of the KNLNS-BBNZ thin films (Figure 1g) show a reflexion around 30° 2θ related to a secondary phase, which increase as the frequency decreases, which was reported in previous works as a pyrochlore phase [12]. The XRD patterns of the KNLNS-BCZ thin films (Figure 1h) present a perovskite structure at both frequencies. However, the peaks between 45° and 47° 2θ present different splits, associated to different crystallographic phases or it suggests a preferent orientation at 5 Hz compared with the samples obtained at 10 Hz.

### B. Microstructural characteristics

SEM micrographs show a strong relationship between the microstructural features and the increase of $PO_2$, which contributes to the material growth rate on the substrate. Fig. 2a-2c of the KNLNS-BBNZ samples and Fig. 2b-2d of the KNLNS-BCZ thin films obtained at 100 and 200 mTorr present wire-shape morphology with random orientation. Previous works reported vertical nanowires with ferroelectric and piezoelectric properties [13], however the random crystal orientation in these materials will diminish these properties. The KLNSN-BBNZ thin film (Fig. 2e) obtained at 300 mTorr, 700 °C, 2 J/cm$^2$, and 10 Hz exhibits random growth in both wire, cube, and amorphous shapes, while the micrograph of the KNLNS-BCZ material (Fig. 2f) shows a homogeneous cubic-shape morphology. The KNLNS-BBNZ thin films obtained at 300 mTorr, 700 °C, 2 J/cm$^2$, and at 10 and 5 Hz, (Fig. 2e-2g) exhibit aleatory growth at both frequencies, which suggest optimizing the deposition parameters to observe piezoelectric properties. Fig. 2f-2h show the KNLNS-BCZ thin films obtained at 10 and 5 Hz, which present homogeneous cubic-shape growth, and high density. Further, the grain size of the thin films fabricated at 10 and 5 Hz are 154 ± 30 nm and 134 ± 26 nm, and their cross-section are 150 nm and 200 nm in thickness, respectively.

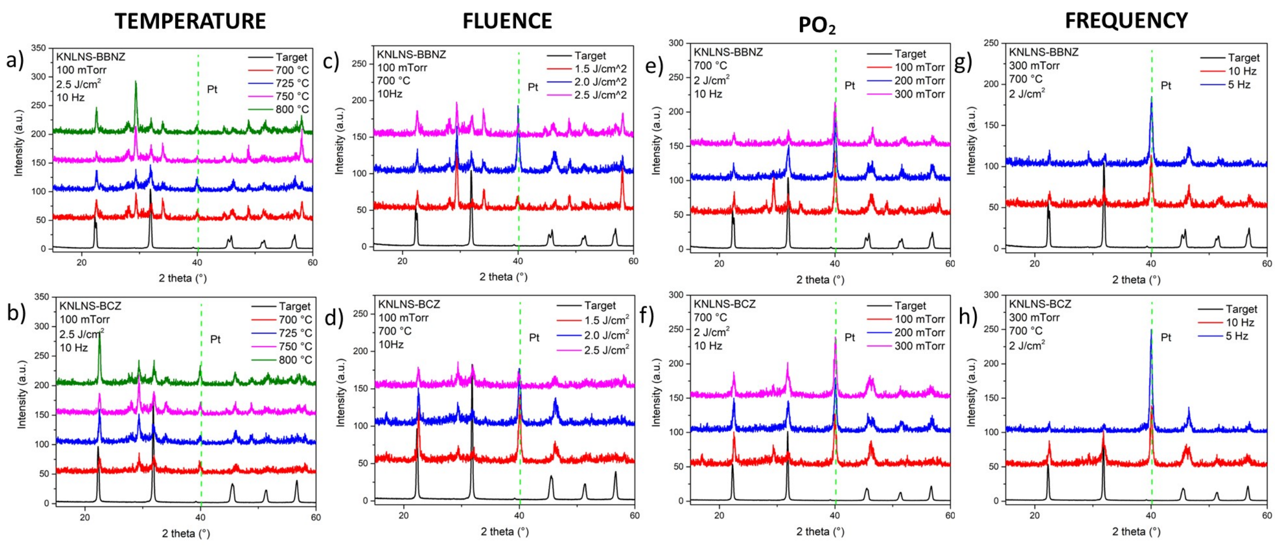


Figure 1. XRD patterns of KNLNS-BCZ (a, c, e, g) and KNLNS-BBNZ (b, d, f, h) thin films.

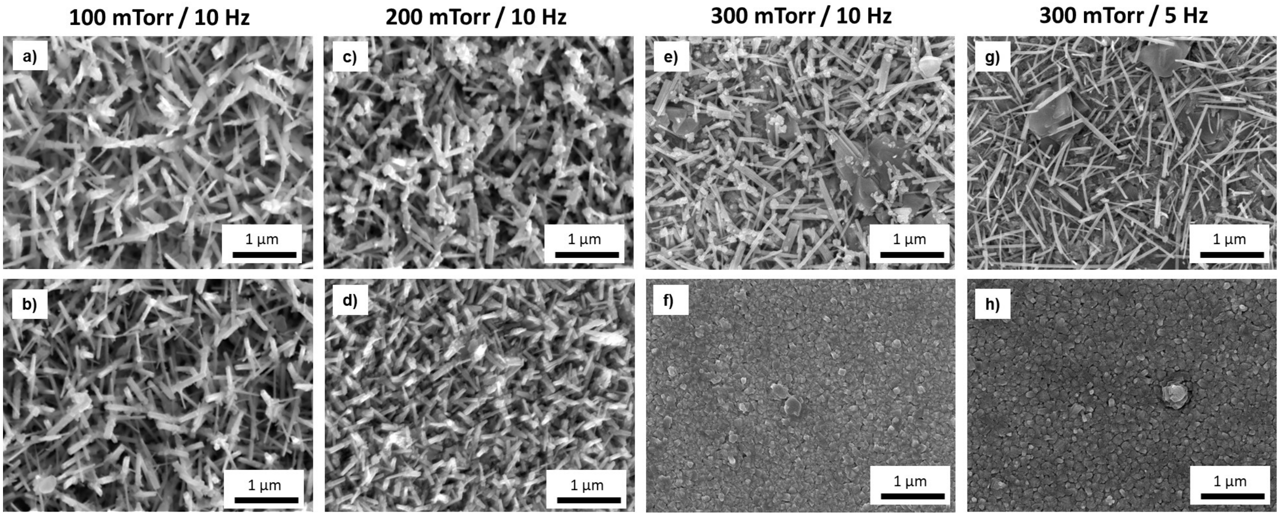


Figure 2. SEM micrograph of KNLNS-BCZ (a, c, e, g) and KNLNS-BBNZ (b, d, f, h) thin films at different $PO_2$.

### C. Ferroelectric and piezoelectric properties

KNLNS-BCZ thin films obtained at 300 mTorr, 700 °C, 2 J/cm$^2$, at 10 and 5 Hz with a pure perovskite structure, high density, homogeneous grain size and flat surface were analysed to determine the piezoelectric properties by Piezoresponse Force Microscopy (PFM). Fig. 3a-3b present the topography of the thin films at 10 and 5 Hz, respectively. According with the colour scale, the samples obtained at 5 Hz show flatter texture compared with those deposited at 10 Hz. Fig. 3c-3d exhibit the amplitude, which is the piezoelectric strain response applying an AC voltage. The dark colour stands for the null amplitude response associated with the domain walls, while the different shades show the piezoelectric response in the domains. Fig. 3e-3f present the phase as the domain angles distribution of the KNLNS-BCZ films. The contrast allows to measure out-of-plane domains, where the dark and bright areas correspond to opposite directions of polarization [14]. Ferroelectric properties were carried out by comparing the first and second harmonic of the amplitude signal. This method compares the electromechanical strain from both the spontaneous polarization (linear) and the induced one (quadratic) [15].

KNLNS-BCZ thin films obtained at 10 and 5 Hz show a strain principally linear, describing a classical ferroelectric material (Fig. 4a-4b). Piezoelectric properties were calculated applying increased voltages and measuring the resonance amplitude in different points. Fig. 4c shows the average displacement at each voltage, from 0.1 to 0.8 V, and the slopes of the linear fits was calculated to obtain the effective piezoelectric coefficient value ($d_{33eff}$) for both samples. The $d_{33eff}$ of KNLSN-BCZ samples fabricated at 10 and 5 Hz were 25.8 and 83.8 pm/V, respectively. Compared with a PZT standard (52.9 pm/V), the KNLNS-BCZ thin film fabricated at 5 Hz shows a higher $d_{33eff}$. The differences in the $d_{33eff}$ value could be attributed to the preferential orientation in samples obtained at 5 Hz.

## IV. Conclusion

Piezoelectric KNLNS-BCZ thin films were obtained by using 300 mTorr (oxygen partial pressure), 700 °C, 2 J/ cm², at 5 and 10 Hz. These thin films presented good piezoelectric response. The $d_{33eff}$ values were 25.8 pm/V and 83.8 pm/V of the samples fabricated at 10 and 5 Hz, respectively.

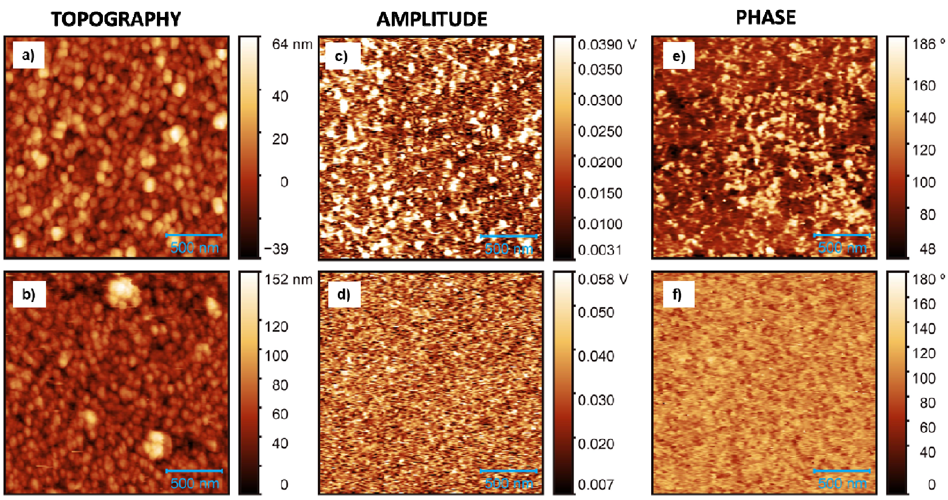


Figure 3. PFM micrography of the KNLNS-BCZ obtained at 10 Hz (a, c, e) and 5 Hz (b, d, f).

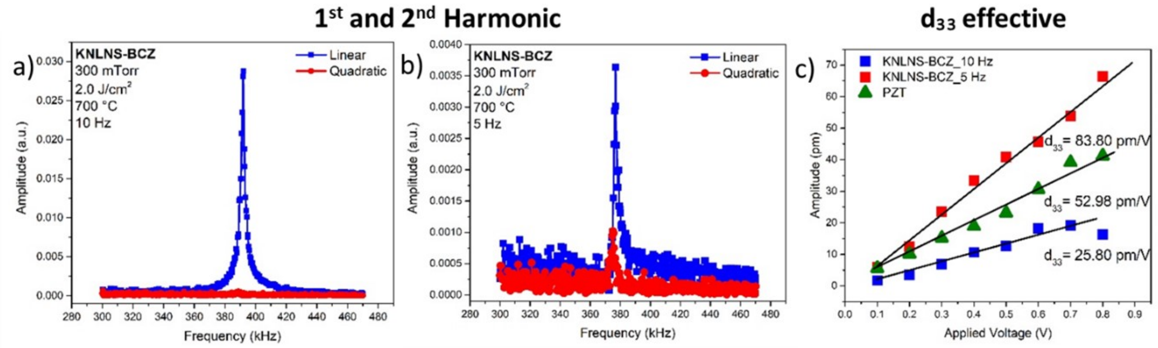


Figure 4. First and second harmonic response of the KNLNS-BCZ fabricated at a) 10 and b) 5 Hz. c) $d_{33eff}$ comparison for the KNLNS-BCZ

KNLNS-BCZ thin films obtained in this work are promising candidates for energy harvesting application due to their high piezoelectric properties, which are close or even superior to those of commercial lead zirconate titanate (PZT) materials.

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