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# Tetragonal tungsten bronze phase thin films in the K-Na-Nb-O system: pulsed laser deposition, structural and dielectric characterizations

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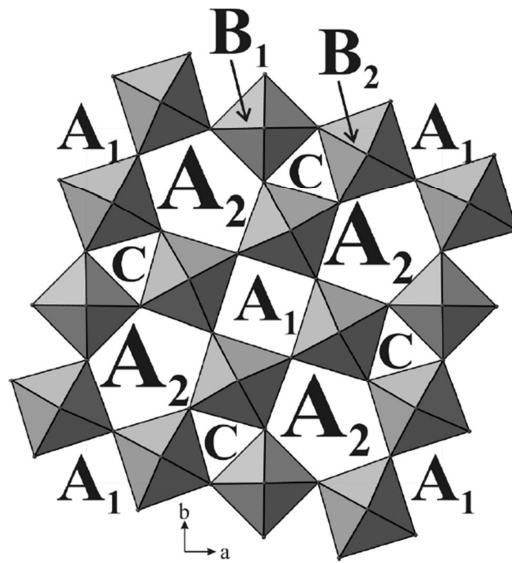
**ABSTRACT**

Pulsed laser deposition parameters have been determined to synthesize pure Tetragonal Tungsten Bronze (TTB) phase thin films in the (K,Na)-Nb-O system (KNN). In relation to the high volatility of alkaline elements, it was found that the target composition and the target-substrate distance are of first importance. The TTB phase was identified by X-ray and electron diffraction and the surface microstructure consisting mainly of nanorods supports the formation of hallmark of the TTB phase. Poly-oriented nanorods have been obtained on both C-plane sapphire and (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si substrates whereas horizontal nanorods oriented along the (*hk*0) planes have been grown on (100) and (110) SrTiO<sub>3</sub>. All the nanorods are parallel together when grown on (110) SrTiO<sub>3</sub> and they present two in-plane orientations rotated of 90° from each other on (100) SrTiO<sub>3</sub>. Dielectric characteristics (dielectric permittivity  $\epsilon_r$ , and loss tangent  $\tan\delta$ ) have been measured at low (1 kHz - 1 MHz) and high (1 GHz - 40 GHz) frequencies, on films deposited on Pt coated silicon and sapphire, respectively. A value of  $\epsilon_r = 200$  at 1 kHz with  $\tan\delta = 0.015$  were measured in a parallel plate capacitor configuration, whereas  $\epsilon_r = 130$  and  $\tan\delta = 0.20$  at 10 GHz were retrieved from transmission lines printed on the KNN TTB thin film grown on C-plane sapphire. Raman investigations of the TTB films were performed in the temperature range 77 - 873 K, confirming the TTB phase formation and the absence of structural transition. Piezoelectric Force Microscopy measurements evidenced a piezoelectric signal although no switching could be performed. However the dielectric measurements, complicated by high leakage currents when a DC voltage was applied, did not evidence any proof of ferroelectricity for the undoped KNN TTB films whereas results reported on other niobates (A,A')<sub>0.6</sub>Nb<sub>10</sub>O<sub>30</sub> (with A: K, Na and A': Sr, Ba, Ca) have shown Curie temperatures, lying between 156°C and

560°C, separating the paraelectric phase (space group:  $P4/mbm$  N°127) and the ferroelectric one (space group:  $P4bm$  N°100).

## 1. INTRODUCTION

Ferroelectric and piezoelectric materials have a wide range of applications from sensors to micro-electro-mechanical systems (MEMS), memory devices and tunable devices, e.g. [1–3]. For decades, the  $PbZr_{1-x}Ti_xO_3$ -based (PZT) material has been the most popular ferroelectric materials [4]. Lately an effort has been made by the scientific community to find a more ecologic and less toxic alternative to this material. Since 2004, the  $K_xNa_{1-x}NbO_3$  perovskite-type material has been established to be a potential substitute for PZT due to its high piezoelectric coefficient  $d_{33}$  (up to 300 pC/N [5]) leading to an important investigation of this phase [6, 7]. The  $K_xNa_{1-x}NbO_3$  perovskite phase has been investigated in bulk [8], thin films [9], single crystals [10] and for photovoltaic applications [11], energy storage [12], luminescence properties [13], sensors [14] or medical imaging [15]. However, in the KNN system, many other phases of potential interest exist without being thoroughly investigated. In many chemical systems, such as K-Nb-O (KN), K-Ta-O, K-Li-Nb-O (KLN) or K-Ta-Nb-O, chemically close to the KNN system, Tetragonal Tungsten Bronze (TTB) phases have been reported either as thin films or bulk [16–20]. The TTB structure can be described along the [001] direction by two cationic octahedral sites B1 and B2 and three cationic tunnels A1, A2 and C, as presented in Figure 1. A1 and A2 sites can be occupied by alkaline metals, alkaline earth, rare-earth and a few other elements. B1 and B2 sites can mostly be occupied by small and highly charged cations, such as  $Nb^{5+}$ ,  $Ta^{5+}$  or  $W^{6+}$ . Finally, the C sites can only be occupied by small cations and are often found to be empty.



**Figure 1.** Projection of the tetragonal tungsten bronze structure along the [001] direction showing the three cationic tunnels A1, A2, and C, and the cationic octahedral sites B1 and B2 [16].

Over the years this crystallographic structure with different cationic sites [21] which authorizes many cationic substitutions and doping possibilities was found to be of interest for exhibiting various properties. For example, in the KLN system, a TTB single crystal study has reported values of piezoelectric coefficient  $d_{33}$  equal to 52 pC/N and ferroelectric polarization  $P_r$  of 25-30  $\mu\text{C}/\text{cm}^2$  [22]. Piezoelectric coefficients  $d_{33}$  were measured reaching 190 pC/N and 114 pC/N, for  $\text{MnO}_2$ -doped and K-doped TTB ceramics in the Sr-Ca-Na-Nb-O system, respectively [23, 24]. In the Sr-Ba-Na-Nb-O system, the TTB phase exhibits a relative permittivity as high as 1600 at 1 kHz [25]. This structure is also studied for optical properties [26] and catalytic activities [27]. In the KNN system, even though the TTB phase has been found as a secondary phase in bulk perovskite [28–30], the pure phase was neither reported nor properly characterized. Some previous works on a modified  $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$  perovskite ceramic have reported that the TTB phase, as a secondary phase, could explain the increase of the piezoelectric properties [29]. The presence of this secondary phase is related to an alkaline deficiency in the ceramic product. Indeed, the  $(\text{K},\text{Na})_6\text{Nb}_{10}\text{O}_{30}$  TTB phase is 40 % lower in alkaline elements than the  $(\text{K},\text{Na})\text{NbO}_3$  perovskite phase.

As no precise description of the KNN system exists when the alkaline/niobium ratio is less than 1, an analogy with the KN system, chemically close to the KNN system has to be made to obtain the TTB phase. In such a system however, various phases are shown to exist with different alkaline/niobium ratios making the pure TTB phase hard to obtain. Nonetheless, the pulsed laser deposition (PLD) technique is suitable for this type of investigation. Indeed, if the method is known to be congruent in the absence of volatile cation, it offers also a great possibility to tune the composition of the films, either by the modification of the target one and/or by the modification of the deposition parameters. Therefore because of the high alkaline (especially potassium) volatility, a thorough investigation of the deposition parameters is requested to grow the pure phase [31].

In this work, KNN thin films were grown by pulsed laser deposition to control pure TTB phase. The films were deposited on different substrates, *i.e.* single crystals (100) and (110) SrTiO<sub>3</sub>, C-plane sapphire and (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si. SrTiO<sub>3</sub> was used here to control the orientation while C-plane sapphire and (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si were used to provide suitable samples for physical measurements. A particular attention was paid to the influence of the deposition parameters on the composition and the structure of the films.

The morphology, structural features and composition have been first investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy and energy-dispersive X-ray spectroscopy (EDXS) analyses. In addition, dielectric properties (relative permittivity and intrinsic loss tangent) have been measured at low (from 1 kHz to 1 MHz) and high (from 1 GHz to 40 GHz) frequencies.

## 2. EXPERIMENTAL SECTION

## 2.1. Elaboration of the KNN targets

The ceramic targets were prepared from KNN powders synthesized by solid state reaction at 940°C for 4 hours in air, from sodium carbonate  $\text{Na}_2\text{CO}_3$  (RP NORMAPUR 99.8%), anhydrous potassium carbonate  $\text{K}_2\text{CO}_3$  (ACROS Organics 99%) and niobium oxide  $\text{Nb}_2\text{O}_5$  (Alfa Aesar 99.5%) powders preliminary mixed in a planetary ball-mill and then calcined. Afterwards 25-mm in diameter targets were sintered either by conventional sintering at 1000°C for 12 h in air, or by Spark Plasma Sintering (SPS, FCT System GmbH). Indeed in the case of the deposition of the perovskite films,  $\text{KNO}_3$  enriched targets are used in order to obtain the final alkaline/niobium ratio of 1. Because of its low melting point, the addition of  $\text{KNO}_3$  in the target favors its sintering [32]. This is not the case for the deposition of TTB thin films which is performed through a non-enriched target. As the target density impacts the overall quality of the thin films and the droplet formation during deposition [33], the alternative SPS method has been used to enhance target density in comparison with targets obtained by conventional sintering. In that case, the powders are placed into a graphite mold which maintains the proper diameter. Graphite foils are introduced between the powder and the mold to facilitate the outmolding. By SPS, a one-step reactive sintering for 10 minutes at 1000°C and about 1 hour of cooling under a 1 bar argon atmosphere leads to a 25-mm-diameter dense KNN ceramic target of which the composition is given in Table 1. A cleaning process of the target of 5 hours at 900°C in air is required to remove the carbon film from the target surface. This step is also used for oxygenation of the ceramic targets. These parameters have been adapted from the work of M. Bah *et al.* [34] and preparation details of each target are summarized in Table 1.

**Table 1.** Chemical composition and sintering details of the different prepared targets. The accuracy of the composition values is 5 %.

| Target number | Targeted composition | Measured composition by SEM EDXS | Sintering technique |
|---------------|----------------------|----------------------------------|---------------------|
|---------------|----------------------|----------------------------------|---------------------|



|           |   |  |  |
|-----------|---|--|--|
| Target T1 | $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$       | $(\text{K}_{0.55}\text{Na}_{0.45})_{0.93}\text{NbO}_x$ | Standard solid-state sintering<br>at 1000°C for 12 h |
| Target T2 | $(\text{K}_{0.5}\text{Na}_{0.5})_{0.7}\text{NbO}_3$ | $(\text{K}_{0.51}\text{Na}_{0.49})_{0.68}\text{NbO}_x$ | Standard solid-state sintering<br>at 1000°C for 12 h |
| Target T3 | $(\text{K}_{0.5}\text{Na}_{0.5})_{0.7}\text{NbO}_3$ | $(\text{K}_{0.49}\text{Na}_{0.51})_{0.54}\text{NbO}_x$ | Spark plasma sintering<br>at 1000°C for 10 minutes   |

## 2.2. Elaboration of the KNN thin films by PLD

Thin films were deposited by PLD technique with a KrF excimer laser (Coherent company, pulse duration 20 ns,  $\lambda = 248$  nm) sets at a fluence of 2-3 J cm<sup>-2</sup>, an energy of 210 mJ and currently at 2 or 4 Hz working frequency. Thin films have been deposited under 0.3 mbar oxygen pressure, at a deposition temperature in the range 600 – 650°C, with a target – substrate distance from 55 to 65 mm. In these conditions the deposition rate is close to 15 nm/min (at 2 Hz) and 30 nm/min (at 4 Hz). In this study the thickness of the films is typically between 250 and 500 nm.

## 2.3. Choice of the substrates

The films were grown on single crystals (100) and (110) SrTiO<sub>3</sub>, C-plane sapphire (i.e. (0001) Al<sub>2</sub>O<sub>3</sub>) and (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si from Crystal GmbH supplier. SrTiO<sub>3</sub> (perovskite structure with a dielectric permittivity  $\epsilon_r$  higher than 300) is a model substrate for the growth of oxides in view to control their orientation. Sapphire is suitable for high frequency applications thanks to its low dielectric permittivity and loss values ( $\epsilon_r \approx 10$  and  $\tan\delta \approx 10^{-4}$  at 10 GHz and room temperature). For the fabrication of the microwave devices, the films have been deposited on 10 mm × 10 mm × 0.5 mm C-plane sapphire substrates. Finally Pt coated silicon (5 mm × 10 mm × 0.7 mm) is well adapted for dielectric measurements in parallel plate capacitor geometry. Each substrate was cleaned in acetone and isopropanol, prior to the deposition step.

## 2.4. Thin films characterizations

The structural characteristics were investigated by X-ray diffraction (XRD) by using a  $\theta$ - $2\theta$  diffractometer (D8 Advance, BRUKER) with a monochromatized  $Cu K_{\alpha 1}$  wavelength ( $\lambda = 1.54056 \text{ \AA}$ ). The surface morphology was observed by scanning electron microscopy (SEM, JSM 7100F, JEOL and MIRA3 Tescan) coupled with an energy dispersive X-ray spectroscopy detector (SEM-EDXS, SDD X-Max 50 mm<sup>2</sup>, Oxford Instruments) to determine the thin film composition. A 5 nm-thick carbon layer was deposited before SEM-EDXS analysis to ensure optimal element detection and especially the potassium one that we have observed to be highly sensitive to charge accumulation effect.

Transmission electron microscopy (TEM) experiments were performed by using a LaB6 JEOL 2100 instrument equipped with an Oxford Aztec 80 mm<sup>2</sup> SDD device for EDXS analysis (TEM-EDXS). Samples were prepared by scratching the thin film from the substrate with a diamond tip and by collecting the so-obtained particles on an amorphous carbon copper grid (Agar). Bright field and dark field transmission electron micrographs, and electron diffraction patterns were recorded using a GATAN Orius 200D CCD (charge coupled device) camera. Schemes of structures were drawn with CrystalMaker software from CIF files of phases under consideration. Simulations of electron diffraction patterns were obtained with the help of CrystalDiffract extension of CrystalMaker.

Raman measurements *versus* temperature (from 77 to 873 K) were performed on TTB-type KNN coated (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si substrates using Renishaw Invia spectrometer and temperature controller (Linkam THMS 600). A green line (514 nm) of Argon-ion laser was taken as the excitation source with a power lower than 1 mW to hedge again heating effect. The scattered light was collected by a  $\times 50$  objective and dispersed by 2400 lines/mm grating in the back-scattering configuration.

Piezoelectric Force Microscopy (PFM) images were obtained with a NTEGRA NT-MDT system using the so-called « Dual Frequency Resonant Tracking » mode, which enables to

enhance the signal to noise ratio by working near the contact resonance frequency of the tip-sample system. Platinum-Iridium tips have been used, with stiffness in the 2-10 N.m<sup>-1</sup> range. In amplitude images, bright zones correspond to higher amplitudes of vibration.

The low frequency dielectric measurements were performed on parallel plate capacitors. Top Au electrodes of surface area  $S$  ( $\varnothing = 300 \mu\text{m}$ , thickness  $t_{\text{Au}} = 200 \text{ nm}$ ) were deposited by magnetron sputtering technique through shadow mask on KNN coated (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si substrates. The capacitance  $C$  and the loss tangent ( $\tan\delta$ ) were measured at room temperature from 1 kHz to 1 MHz with an AC driving voltage  $V_{\text{ac}} = 125 \text{ mV}$ , using an Agilent 4294A impedancemeter. The dielectric permittivity  $\epsilon_r$  of each sample was retrieved from the measured capacitance ( $C$ ) using the parallel plate capacitor formula, where  $t_{\text{KNN}}$  is the thickness of the KNN film:

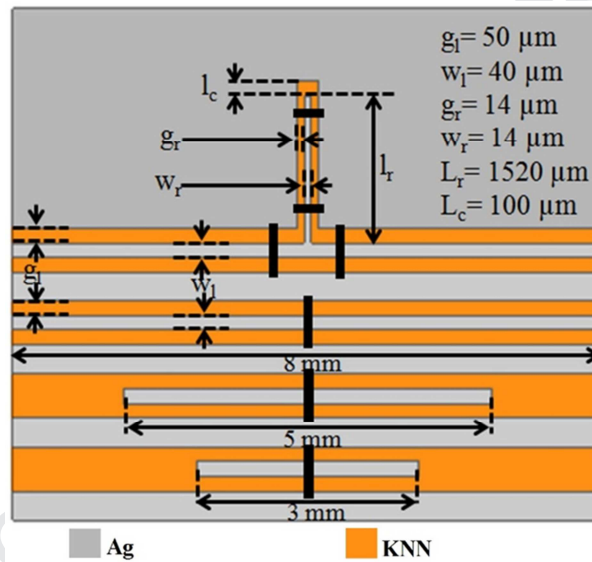
$$\epsilon_r = \frac{C \times t_{\text{KNN}}}{\epsilon_0 \times S} \quad (1)$$

## 2.5. Microwave devices for dielectric characterization at microwave frequencies

The dielectric characteristics and frequency tunability of the KNN TTB thin films were investigated using coplanar waveguide (CPW) and transmission lines devices designed with a 3-D commercial electromagnetic software (Ansys HFSS<sup>TM</sup>). Three 50- $\Omega$  lines (8 mm, 5 mm and 3 mm long) with a conductor width  $w_l = 40 \mu\text{m}$  surrounded by a gap  $g_l = 50 \mu\text{m}$  (Figure 2) were implemented to retrieve the thin films dielectric characteristics ( $\epsilon_r$ ,  $\tan\delta$ ), from the microwave measurements. A CPW quarter-wavelength open-ended stub resonator was also designed to operate in X-band. Its resonance frequency  $F_r$  depends upon the stub length  $L_r$  and the effective permittivity  $\epsilon_{\text{eff}}$  of the heterostructure, as follows:

$$F_r = \frac{c}{4L_r \sqrt{\epsilon_{\text{eff}}}} \quad (2)$$

where  $c$  is the speed of light in vacuum. The devices were fabricated from a 2  $\mu\text{m}$ -thick silver overlayer grown on a 5 nm-thick titanium underlayer deposited by RF magnetron sputtering at room temperature. The silver thickness is three times larger than the skin depth value ( $\delta = 0.64 \mu\text{m}$ ) at 10 GHz. Note that the ultrathin titanium film is used here only to ensure the strong adhesion of the silver film onto the ferroelectric oxide. Standard photolithography and wet etching processes were implemented to pattern the devices. Gold wire bondings (15  $\mu\text{m}$ -diameter and 250  $\mu\text{m}$ -length) were used to enforce the equipotential condition on both CPW grounds and prevent from the excitation of parasitic slotline mode (Figure 2).



**Figure 2.** Layout and dimensions of the CPW devices.

Microwave measurements at room temperature and from 20°C to 240°C were carried out through a probe station coupled to a vector network analyzer (VectorSTAR MS4644B, ANRITSU) from 1 to 40 GHz under an external DC bias voltage range from 0 to 150 V, which corresponds to a maximal static electric field  $E_{bias}$  equal to 90 kV/cm for the stub resonator and 27 kV/cm for the transmission lines. The measured gap dimensions ( $g_r \approx 16 \mu\text{m}$  and  $g_l \approx 52 \mu\text{m}$ ) are slightly larger than the nominal ones due to the inherent overetching of the used wet etching process. Further details are reported elsewhere [35].

### 3. RESULTS AND DISCUSSION

#### 3.1. Influence of the deposition parameters to grow pure KNN TTB thin films on the various substrates

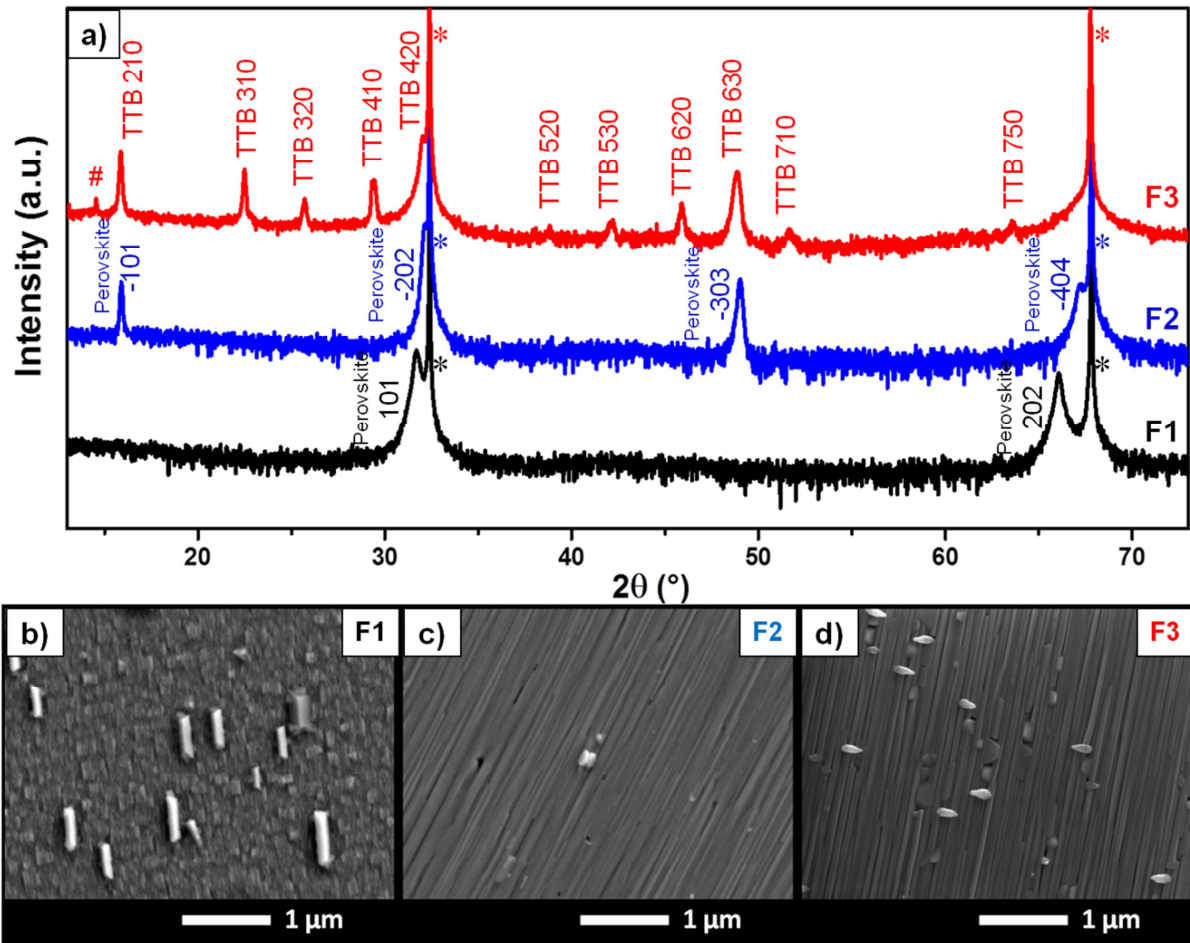
From a previous study [32] it has been shown that among the various deposition parameters, the target composition, the deposition temperature and the target – substrate distance  $D$  have a strong impact on the thin films composition and crystallization, explaining their accurate assessment impact. Table 2 gathers the deposition parameters of the films considered in the present study. Since a film thickness of about 250 nm was obtained with the laser frequency of 2 Hz, the frequency was increased to 4 Hz to achieve a thickness near 500 nm, more suitable for the high frequency reconfigurable devices [47].

The samples labelled in Table 2 are the most significant in view to control the TTB single phase in the KNN system.

**Table 2.** Summary of deposition parameters and different characteristics of the thin films. The accuracy of the composition values is 5 %.

| Thin film | Substrate   | Target | Freq. (Hz) | Temp. (°C) | Dist. target-sub. (mm) | Identified phase by XRD                                 | Measured composition (EDXS)   |
|-----------|---|--------|------------|------------|------------------------|---|---|
| F1        | (110)SrTiO <sub>3</sub>                             | T1     | 2          | 600        | 55                     | Perovskite  | TEM<br>(K <sub>0.4</sub> Na <sub>0.6</sub> ) <sub>0.92</sub> NbO <sub>x</sub>   |
| F2        | Nb:(110)SrTiO <sub>3</sub>                          | T1     | 2          | 650        | 55                     | Perovskite  | TEM<br>(K <sub>0.14</sub> Na <sub>0.86</sub> ) <sub>0.79</sub> NbO <sub>x</sub> |
| F3        | Nb:(110)SrTiO <sub>3</sub>                          | T2     | 2          | 600        | 55                     | TTB<br>+ K <sub>4</sub> Nb <sub>6</sub> O <sub>17</sub> | TEM<br>(K <sub>0.58</sub> Na <sub>0.42</sub> ) <sub>0.62</sub> NbO <sub>x</sub> |
| F4        | (110)SrTiO <sub>3</sub>                             | T3     | 4          | 650        | 65                     | TTB   | SEM<br>(K <sub>0.45</sub> Na <sub>0.55</sub> ) <sub>0.44</sub> NbO <sub>x</sub> |
| F5        | (001)SrTiO <sub>3</sub>                             | T3     | 4          | 650        | 65                     | TTB   | SEM<br>(K <sub>0.47</sub> Na <sub>0.53</sub> ) <sub>0.43</sub> NbO <sub>x</sub> |
| F6        | (111)Pt/TiO <sub>2</sub> /SiO <sub>2</sub> /(001)Si | T3     | 4          | 650        | 60                     | TTB<br>+ KNb <sub>3</sub> O <sub>8</sub>                | SEM<br>(K <sub>0.49</sub> Na <sub>0.51</sub> ) <sub>0.46</sub> NbO <sub>x</sub> |
| F7        | C-plane sapphire                                    | T3     | 4          | 650        | 65                     | TTB   | SEM<br>(K <sub>0.49</sub> Na <sub>0.51</sub> ) <sub>0.41</sub> NbO <sub>x</sub> |
| F8        | C-plane sapphire                                    | T3     | 4          | 650        | 60                     | TTB   | SEM<br>(K <sub>0.49</sub> Na <sub>0.51</sub> ) <sub>0.40</sub> NbO <sub>x</sub> |
| F9        | C-plane sapphire                                    | T3     | 4          | 650        | 55                     | TTB<br>+ KNb <sub>3</sub> O <sub>8</sub>                | SEM<br>(K <sub>0.50</sub> Na <sub>0.50</sub> ) <sub>0.45</sub> NbO <sub>x</sub> |

**First the role of the target composition has been investigated.** Since data have not been yet reported on the TTB phase in the KNN system, the knowledge about the KN system [31] chemically close to the KNN one, has been therefore considered. With the aim to obtain a thin film composition close to  $(K_xNa_{1-x})_6Nb_{10}O_{30}$  and while taking into account the alkaline elements volatility during the PLD process [31, 32], the  $K_{0.5}Na_{0.5}NbO_3$  target (T1) has been first used. As shown in Figure 3a, XRD pattern of the F1 film, grown on (110)SrTiO<sub>3</sub> at 600°C, displays the  $K_{0.4}Na_{0.6}NbO_3$  perovskite phase peaks with a (101) preferential growth, in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) file #00-061-0310 (space group: *Pm* (6);  $a = 3.99628 \text{ \AA}$ ,  $b = 3.93776 \text{ \AA}$ ,  $c = 3.99335 \text{ \AA}$ ,  $\beta = 90.3398^\circ$ ). The SEM micrograph (Figure 3b) shows a F1 film made of crystallites with rectangular shape of about  $300 \text{ nm} \times 100 \text{ nm}$ , aligned in the plane along the  $\langle 100 \rangle$  axis of the substrate. A few crystals (white contrast) with higher size are also observed. The composition determined by SEM-EDXS  $(K_{0.4}Na_{0.6})_{0.92}NbO_3$  is in good agreement with the XRD results and the expected depletion in alkaline elements, especially potassium, during the PLD process. Nevertheless, this depletion is not sufficient to achieve the composition range of the TTB phase.



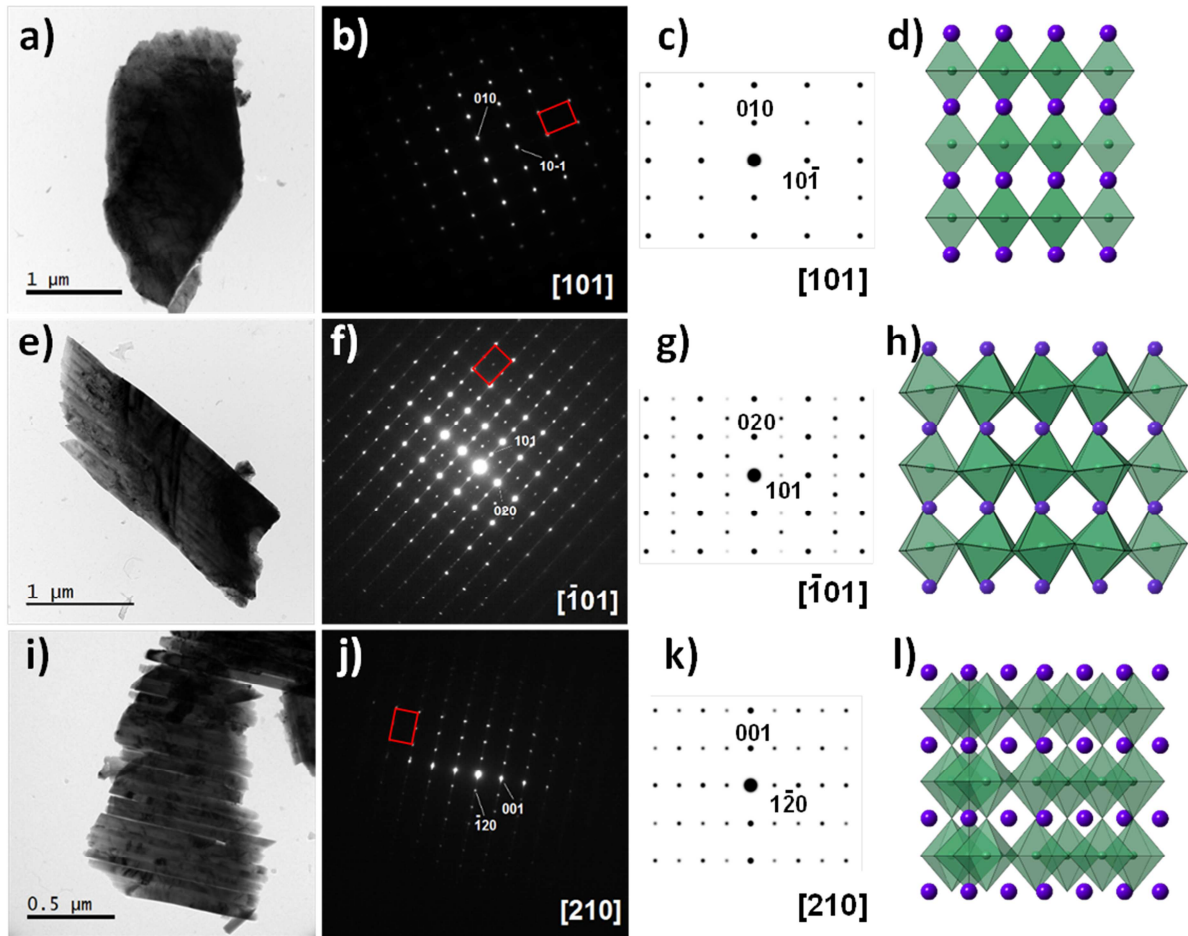
**Figure 3.** XRD patterns of F1, F2, F3 films (#:  $K_4Nb_6O_{17}$  phase, \*: substrate) (a). Scanning electron micrographs of F1, F2 and F3 films (b-d).

A second film, namely F2, was grown on the Nb:(110)SrTiO<sub>3</sub> from the same target at higher temperature. The related composition is  $(K_{0.14}Na_{0.86})_{0.79}NbO_x$  with a lower amount of alkaline elements, but still too high for the expected composition. The depletion in potassium is particularly high in this sample. Among the several perovskite phases known in this part of the  $K_xNa_{1-x}NbO_3$  solid solution, only  $K_{0.1}Na_{0.9}NbO_3$  (JCPDS files # 01-074-2025, space group:  $Pm$  (6);  $a = 7.8720 \text{ \AA}$ ,  $7.7920 \text{ \AA}$ ,  $7.8632 \text{ \AA}$ ,  $\beta = 90.479^\circ$ ) fits with the XRD pattern, with a  $(\bar{1}01)$  preferential growth (Figure 3a). The SEM micrograph shows a film made of very long (several microns) and thin parallel crystallites (50-100 nm wide)(Figure 3c).

To favor the growth of the TTB phase, the alkaline target composition was further decreased down to  $(\text{K}_{0.5}\text{Na}_{0.5})_{0.7}\text{NbO}_3$  (target T2). The film obtained at  $600^\circ\text{C}$  using this target (F3) leads to the formation of the TTB phase on  $\text{Nb}:(110)\text{SrTiO}_3$  as displayed by XRD (Figure 3a). On this pattern, only  $\{hk0\}$  peaks of the TTB phase are present indicating preferential growth according to the JCPDS file #01-087-1856 of the  $\text{K}_6\text{Nb}_{10.88}\text{O}_{30}$  TTB phase (space group:  $P4/mbm$  (127);  $a = 12.5820 \text{ \AA}$ ,  $c = 3.9920 \text{ \AA}$ ). A minor peak at  $2\theta = 14.54^\circ$  indicates the presence of the  $\text{K}_4\text{Nb}_6\text{O}_{17}$  phase (JCPDS file #01-076-0977) as a secondary phase. The corresponding SEM micrograph shows long (several microns) and thin crystallites (50 nm wide). Some other crystallites exhibit out-of-plane short nanorod shape (white contrast on the SEM micrograph). The  $(\text{K}_{0.58}\text{Na}_{0.42})_{0.62}\text{NbO}_x$  composition is therefore close to the expected one. Morphology of the F2 (perovskite phase) and F3 (TTB phase) films being very similar, further transmission electron microscopy and electron diffraction experiments were performed to get in-plane information.

Figure 4 presents bright field micrographs and electron diffraction patterns (EDP) along the normal of F1, F2 and F3 films. EDP of the  $(\text{K}_{0.4}\text{Na}_{0.6})_{0.92}\text{NbO}_3$  perovskite phase (film F1) displays a primitive rectangular cell, which corresponds to the  $[101]$  zone axis of a pseudo-cubic cell with lattice parameters close to  $4 \text{ \AA}$  (Figure 4b), as expected from the simulated EDP (Figure 4c). For the purpose of comparison, the  $(110) \text{SrTiO}_3$  cell was drawn in red in all the EDPs of Figure 4. The perovskite phase presents therefore epitaxial relationships with the  $(110) \text{SrTiO}_3$  substrate, whose cell has roughly the same dimensions. The related relationships are:  $[101]_{\text{KNN}} // [101]_{\text{STO}}$ ,  $(010)_{\text{KNN}} // (100)_{\text{STO}}$ ,  $(10\bar{1})_{\text{KNN}} // (10\bar{1})_{\text{STO}}$ . Comparison between image and diffraction pattern enable to determine the elongation direction of the small rectangular crystals that form the film, namely the  $[010]$  direction. This corresponds to the elongation direction of the distorted octahedral, as drawn in Figure 4d.





**Figure 4.** Bright field TEM micrographs, experimental and theoretical electron diffraction patterns and corresponding schemes of the KNN structures under consideration of perovskite F1 film (a,b,c,d), perovskite F2 film (e,f,g,h) and TTB F3 film (i,j,k,l). Red rectangle: scheme of the SrTiO<sub>3</sub> cell.

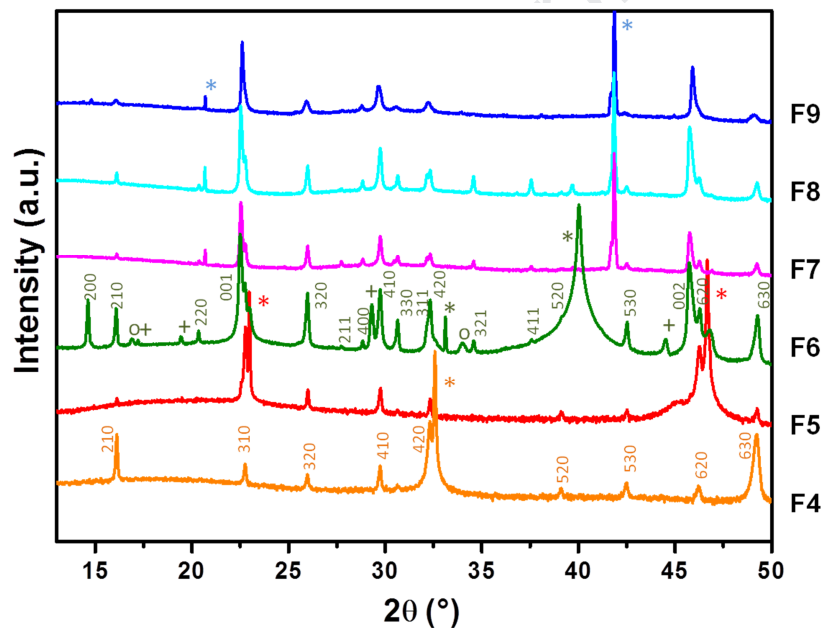
The EDP of the  $K_{0.14}Na_{0.86}NbO_x$  phase (film F2), displayed in Figure 4f, shows a rectangular cell corresponding to a pseudo-cubic phase with lattice parameters twice the ones of a simple perovskite cell (simulated in Figure 4g). Similarly to the previous perovskite phase, the epitaxial relationships are:  $[\bar{1}01]_{KNN} // [101]_{STO}$ ,  $(100)_{KNN} // (100)_{STO}$ ,  $(101)_{KNN} // (10\bar{1})_{STO}$ . Comparison between the image of the long crystals (Figure 4c) and EDP indicates a [010] elongation direction. This corresponds to the elongation direction of the octahedra in the phase as well (Figure 4h).

EDP of the TTB phase (film F3) along the [210] zone axis is displayed in Figure 4j. As expected, the pattern consists of a primitive rectangular along the above direction (simulation in Figure 4k). Comparison with the substrate cell (red rectangle in Figure 4j) provides the following epitaxial relationships:  $[210]_{\text{TTB}}//[101]_{\text{STO}}$ ,  $(001)_{\text{TTB}}//(100)_{\text{STO}}$ ,  $(\bar{1}20)_{\text{TTB}}//(10\bar{1})_{\text{STO}}$ . The parallelepiped-shape long crystal elongation is along the [001] direction, as commonly observed for TTB phases [16, 36]. As for the two previous phases, this direction corresponds to a slight distortion of the octahedra. These results agree with the most intense peaks of the TTB film on the XRD pattern (Figure 3a) which correspond to the (210), (420) and (630) reflections. From the XRD ( $hk0$ ) peak position, the lattice parameter  $a$  was computed ( $a = 12.483 \pm 0.005 \text{ \AA}$ ), and from the EDP, the lattice parameter  $c$  is about  $3.99 \pm 0.05 \text{ \AA}$ . Along the two in-plane directions, the substrate-film cells mismatches are respectively  $\delta_1 = [d(100)_{\text{STO}} - d(001)_{\text{TTB}}]/d(100)_{\text{STO}} = -2.17 \%$  and  $\delta_2 = [d(101)_{\text{STO}} - d(120)_{\text{TTB}}]/d(101)_{\text{STO}} = -1.09 \%$ .

To enhance the stabilization of the KNN TTB phase thin films by decreasing the alkaline content, films (F4 to F9) were then deposited at temperature  $T = 650^\circ\text{C}$  by using a PLD target sintered by SPS with the  $(\text{K}_{0.49}\text{Na}_{0.51})_{0.54}\text{NbO}_x$  composition (target T3).

**Samples were also grown with various target-substrate distances** on C-plane sapphire substrate, *i.e.*  $D = 65 \text{ mm}$  (film F7),  $D = 60 \text{ mm}$  (film F8),  $55 \text{ mm}$  (film F9) and  $50 \text{ mm}$  (not shown). For F7 and F8 films, similar XRD patterns and surface morphologies were observed (see Figure 5 and Figure 6 and related discussion hereafter). For F9 film however, a slight amount of the  $\text{KNb}_3\text{O}_8$  phase is noticed on XRD pattern. Independently of the substrate type, a target-substrate distance under  $60 \text{ mm}$  has resulted in the formation of secondary phases. In the following work this distance has been selected to be equal at least to  $60 \text{ mm}$ .

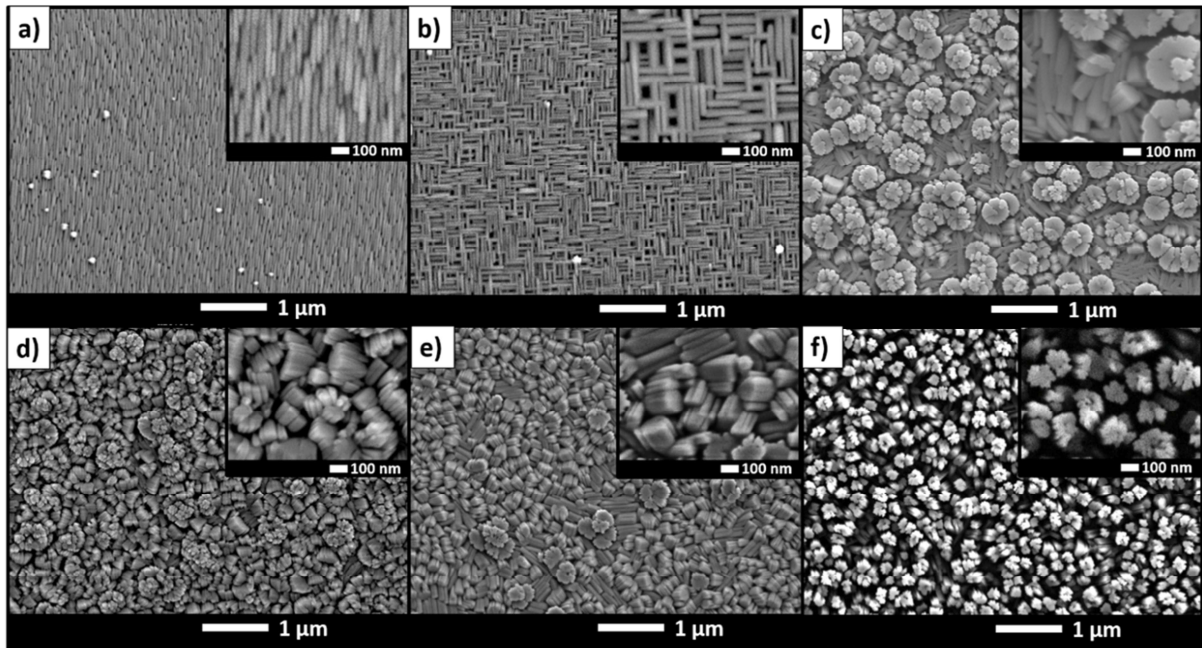
In order to control the orientation two films were deposited on SrTiO<sub>3</sub> substrates, F4 on (110)SrTiO<sub>3</sub> and F5 on (001)SrTiO<sub>3</sub>. In both cases, pure TTB coatings were obtained. XRD pattern of the film F4 presents pure  $\{hk0\}$  TTB phase peaks with a strong (210) preferential orientation (Figure 5), in agreement with XRD and TEM observations performed on F3. Nonetheless, SEM micrograph F4 shows crystallites with parallelepiped-shape and shorter than for film F3 (about 50 nm wide and up to 700 nm long, Figure 6a). It could be noted that SEM images of the films synthesized from the T3 target do not exhibit any additional outgrowths or droplets that can often be observed, especially with targets of the KNN system phases which are difficult to densify by conventional synthesis.



**Figure 5.** XRD patterns of TTB films grown on (110)STO (film F4, D = 65 mm), (001)STO (film F5, D = 65 mm), (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si (film F6, D = 60 mm) and C-plane sapphire (film F7, D = 65 mm), (film F8, D = 60 mm), (film F9, D = 55 mm) (\*: substrates; o: KNb<sub>3</sub>O<sub>8</sub>; + K<sub>3</sub>Nb<sub>7</sub>O<sub>19</sub>) (logarithmic scale).

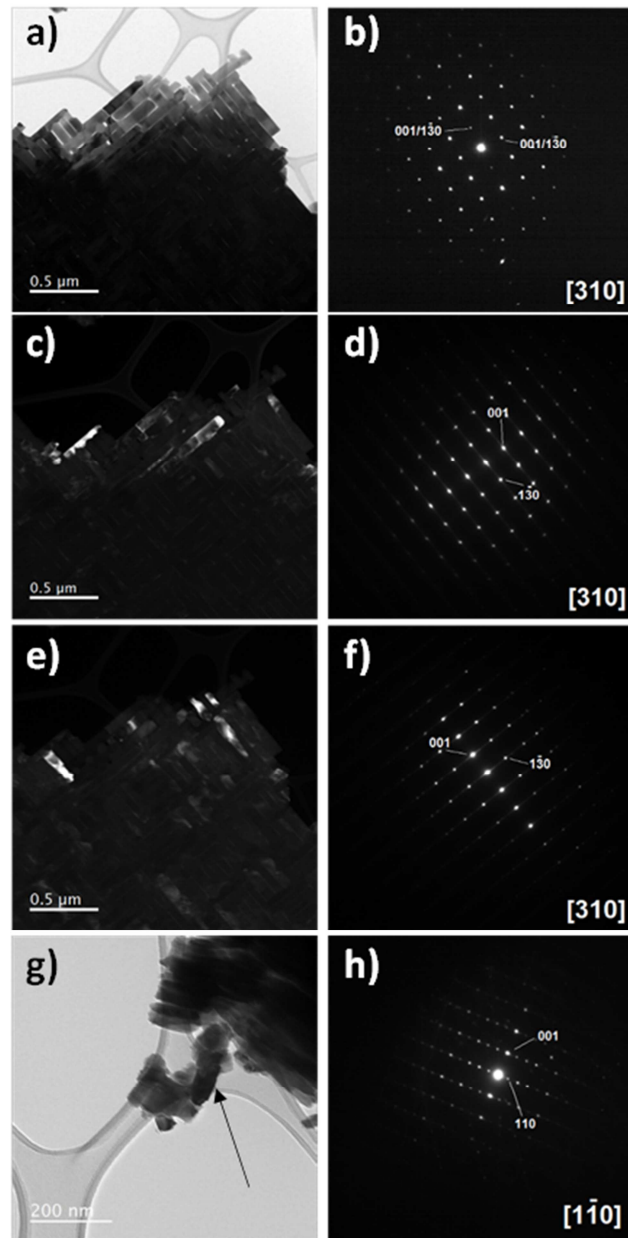
Regardless of the SrTiO<sub>3</sub> substrate orientation, nanorods present a quite perfect in-plane orientation with almost no vertical nanorods growing along the *c*-axis parallel to the normal of the substrate. On (110) SrTiO<sub>3</sub>, the nanorods present a (210) out-of-plane main orientation

and are all growing parallel to each other along the same in-plane direction (film F4, Figure 6a), in line with a lowering of the mismatch between film and substrate cells along this direction (see discussion on the epitaxial relationships for F3). On the (001) SrTiO<sub>3</sub> substrate (film F5, figure 6b), the nanorods are growing along two in-plane directions with a 90° angle to each other (Figure 6b) with a (310) out-of-plane preferential orientation. Corresponding EDP registered along the [310] zone axis (Figure 7b) shows a pseudo-cubic array of reflections. The (001)SrTiO<sub>3</sub> substrate involves this particular orientation due to the small mismatch between the cubic (100) × (010) cell of SrTiO<sub>3</sub> with  $d_{100} \times d_{010} = 3.905 \text{ \AA} \times 3.905 \text{ \AA}$  dimensions and the pseudo-cubic cell (001) × (1 $\bar{3}$ 0) of the TTB phase with  $d_{001} \times d_{310} = 3.99 \text{ \AA} \times 3.937 \text{ \AA}$  dimensions. These experimental values were determined from the XRD (310) peak position and from the EDP (001) reflection of the individual nanorods registered in microdiffraction conditions (Figures 7d and 7f), respectively. Mismatches between the substrate and the film cells are respectively  $\delta_1 = [d(100)_{\text{STO}} - d(001)_{\text{TTB}}] / d(100)_{\text{STO}} = -2.17 \%$  and  $\delta_2 = [d(010)_{\text{STO}} - d(130)_{\text{TTB}}] / d(010)_{\text{STO}} = -0.84 \%$ . Note that, in contrast to (110)SrTiO<sub>3</sub> substrate, the square cell of the (001)SrTiO<sub>3</sub> plane leads to equivalent mismatches at 90° from each other, explaining the growth of the KNN TTB nanorods along two in-plane orientations as observed in Figure 6b. The corresponding lattice parameters were computed as  $a = 12.453 \pm 0.005 \text{ \AA}$  (XRD) and  $c = 3.99 \pm 0.05 \text{ \AA}$  (EDP).



**Figure 6.** Scanning electron micrographs of the TTB films grown on: (a) (110)STO (film F4, D = 65 mm); (b) (001)STO (film F5, D = 65 mm); (c) (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si (film F6, D = 60 mm); (d) C-plane sapphire (film F7, D = 65 mm); (e) C-plane sapphire (film F8, D = 60 mm), (f) C-plane sapphire (film F9, D = 55 mm).

In addition, microdiffraction pattern of the individual nanorods shows diffuse scattering lines along the  $[1\bar{3}0]$  growth direction, indicating some planar disorder perpendicularly to this direction. By dark field method in 2-beams conditions, it was also possible to enlighten individual nanorods along the two different in-plane directions by selecting corresponding diffraction reflections (Figure 7c and 7e).



**Figure 7.** (a) Bright field TEM micrograph of the TTB films grown on (001)STO (film F5); (b) corresponding selected area EDP along the [310] zone axis; (c,e) Dark field TEM micrographs showing individual nanorods growing along the two in-plane directions; (d,f) Microdiffraction EDP of each nanorod variant along the [310] zone axis; (g,h) Bright field TEM micrograph and EDP along the  $[1\bar{1}0]$  zone axis of the TTB film grown on C-plane sapphire (film F7). The arrow displays the crystallite corresponding to the EDP.

**Thin films were also deposited on Pt and sapphire** substrates to perform dielectric characterizations (at low frequency and at microwaves, respectively). XRD pattern of the thin film grown on (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si (film F6) indicates a polycrystalline growth (*i.e.*

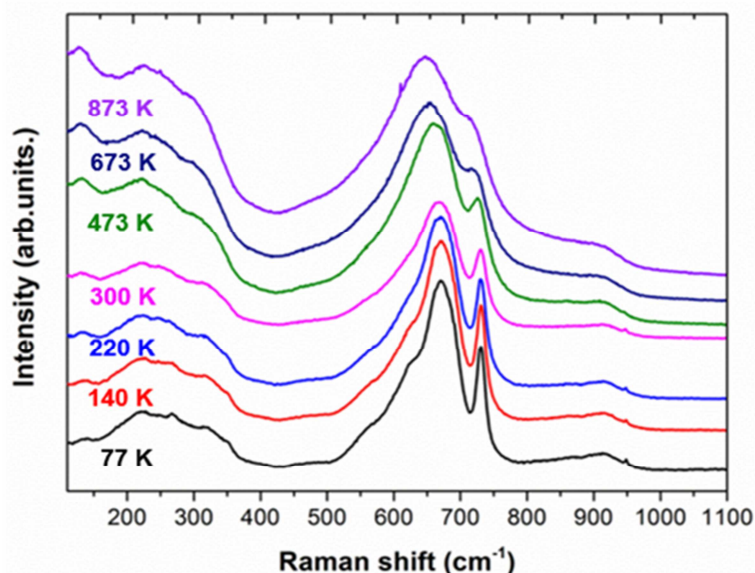
random orientation) with a (001) preferential orientation of the nanorods (Figure 5). In that case, the nanorods have grown as thin rod aggregates attached together by their longer edge, as observed on SEM micrograph (Figure 6c). The (001) preferential orientation is consistent with the presence of vertical agglomerated nanorods forming a flower-like microstructure. XRD pattern also exhibits minor secondary phases identified as  $\text{KNb}_3\text{O}_8$  and  $\text{K}_3\text{Nb}_7\text{O}_{19}$  (JCPDS files # 01-075-2182 and #00-084-0812, respectively). The presence of secondary phases in films grown on Pt coated silicon, in contrast to those grown on  $\text{SrTiO}_3$ , could be explained by its higher thermal conductivity that increases the substrate surface temperature for the same deposition temperature. It is assumed that these phases presence has a minor impact on the thin film properties due to their small amount (Figure 5).

On C-plane sapphire, XRD patterns on F7 and F8 films show pure TTB phase (Figure 5). For both samples, those patterns exhibit a similar (001/310) preferential growth. TEM experiments performed on the F7 film confirm the elongation direction of nanorods along [001] direction (Figure 7g and 7h). EDXS analyses indicate a lower alkaline elements amount in the TTB nanorods compared with those grown on  $\text{SrTiO}_3$  (Table 2). However on both substrates, the films present a sodium/potassium ratio close to 1 and an alkaline elements/niobium ratio slightly lower than the nominal composition  $(\text{K,Na})_{0.6}\text{Nb}_{1.1}\text{NbO}_3$ , indicating that some cationic sites are therefore partially filled.

### 3.2. Investigation of the structural characteristics by Raman spectroscopy

Figure 8 shows Raman spectra of the TTB thin film grown on (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si substrate (film F6). At room temperature, the spectra present typical signature of TTB phases compared with that reported for isostructural system [37–41], in agreement with X-ray diffraction and TEM analyses. Modes at 670 cm<sup>-1</sup> and 731 cm<sup>-1</sup> are assigned to the Nb–O stretching vibrations in the [NbO<sub>6</sub>] octahedra, and modes located in the 70 to 400 cm<sup>-1</sup> range

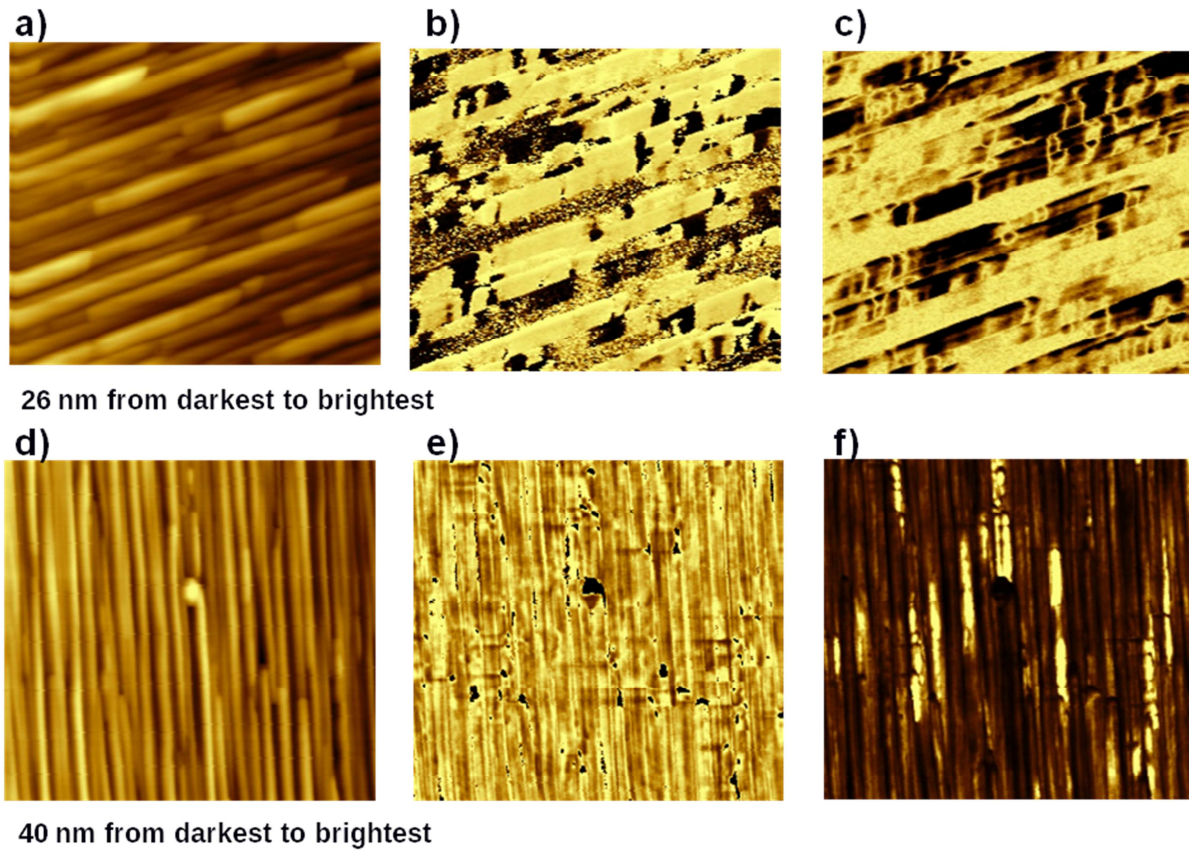
is attributed to the O–Nb–O bending modes between adjacent  $[\text{NbO}_6]$  octahedra, as observed on other TTB niobates. The broad peaks with important contribution overlap, especially at low frequency region ( $< 400 \text{ cm}^{-1}$ ), are characteristic of the TTB structure with cationic disorder in A1, A2 and C sites. These effects make the assignment of Raman lines hardly attainable, and so, it is impossible to distinguish unambiguously a centrosymmetrical structure from a non-centrosymmetrical one. Temperature-dependent spectra show neither significant shift nor anomaly in peak position and splitting or number modes change between 77 K and 873 K. This result strongly suggests a stable film structure and no clear evidence of any structural transition occurs over the entire temperature range studied.



**Figure 8.** Raman spectra of the TTB thin film deposited on (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si (film F6) at various temperatures (from 77 K to 873 K)

### 3.3. Investigation by Piezoelectric Force Microscopy





**Figure 9.** PFM of perovskite (F2) and TTB (F3) films: (a,d) topography; (b,e) phase; (c,f) amplitude.  $2\ \mu\text{m} \times 2\ \mu\text{m}$  size images

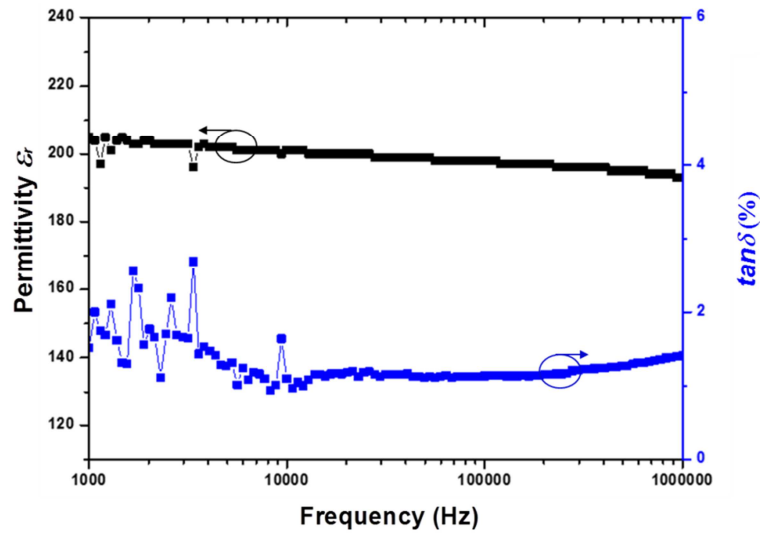
Piezoelectric Force Microscopy performed in topography mode on F2 and F3 films shows the typical morphologies of the perovskite and TTB-type KNN phases grown on  $(110)\text{SrTiO}_3$  (Figure 9a and 9d). In piezoresponse mode (Figure 9b, 9c, 9e and 9f), a clear contrast is observed in both cases, with a heterogeneous piezoelectric response: some grains show a strongest response (bright areas in Figure 9c and 9f) compared with others, with quasi-null amplitude response (dark areas in Figure 9c and 9f). In the case of the perovskite phase (Figure 9a-9c), where the PFM phase signal presents opposite directions of vertical polarization (the histogram of phase values (not shown) is composed of two peaks separated by  $180^\circ$ ), this can be explained by a polarization direction in the orthorhombic cell with various directions relatively to the preferential orientation. Indeed the polarization in this kind of perovskite is aligned along the diagonal of the facets of the pseudo-cubic cell, *i.e.* the

$\langle 110 \rangle$  directions. In the present case, these directions correspond either to the normal direction or to the in-plane direction. Concerning the TTB phase, it is expected that the polarization direction is parallel to the [001] direction, therefore to the nanorod growth direction. Whereas a piezoresponse was observed, it has not been possible to reverse the signal by applying a reversed DC bias voltage. This experimental result is assigned to high leakage currents that make impossible to reach the coercive electric field without destroying the sample by Joule effect. In the case of the TTB phase whose properties are not fully established, another possibility concerns the piezoelectric response without ferroelectricity of the sample, at least at room temperature.

### 3.4. Dielectric characteristics

#### 3.4.1. Low frequency measurements

The dielectric characteristics ( $\epsilon_r$  and  $\tan\delta$ ) at low frequencies were retrieved from the KNN TTB thin film (F6) grown on (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si substrate. No frequency dispersion of the dielectric characteristics was observed from 1 kHz to 1 MHz with a permittivity value  $\epsilon_r \approx 200$  and  $\tan\delta \approx 1.5\%$  (Figure 10). The recorded permittivity values are in the same range as to those of other TTB thin films, for instance  $\epsilon_r \approx 400$  for K<sub>3</sub>Li<sub>2</sub>Nb<sub>5</sub>O<sub>15</sub> epitaxial films [42] and  $\sim 150$  for Ba<sub>2</sub>LnFeNb<sub>4</sub>O<sub>15</sub> (Ln = La, Nd, Eu) polycrystalline films [43], or to other values that can be found for ferroelectric thin films or dielectric relaxors as in the Bi-Zn-Nb-O system [44]. It has to be pointed out that polarization versus electric field measurements have been attempted. However, the high leakage currents make difficult the measurements under DC electric field and it was not possible to observe hysteric loop with saturation of the polarization.



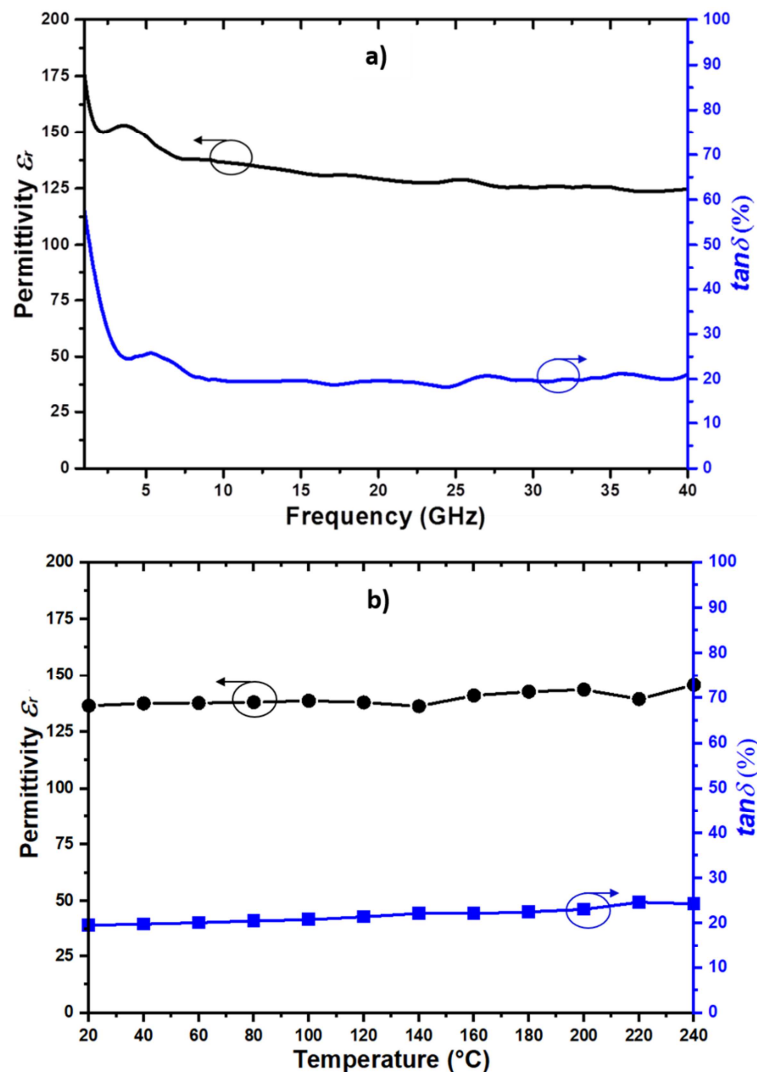
**Figure 10.** Variation of the dielectric characteristics (permittivity  $\epsilon_r$  and loss  $\tan\delta$ ) at low frequencies of the TTB thin film (F6) deposited on (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si.

### 3.4.2. High frequency measurements

The dielectric characteristics ( $\epsilon_r$  and  $\tan\delta$ ) at high frequencies were retrieved from the KNN TTB thin film (F8) grown on C-plane sapphire substrate. The values were obtained using the measured reflection ( $S_{11}$ ) and transmission ( $S_{21}$ ) coefficients of the transmission lines. TTB thin film exhibits a permittivity  $\epsilon_r = 135$  at 10 GHz, 130 at 20 GHz, and 125 at 30 GHz showing a good stability versus frequency (Figure 11a). Even though the literature does not present many microwave dielectric characterizations of the TTB phases, permittivity values close to 130 have also been reported for other materials [45, 46]. Nevertheless, these values remain lower than those retrieved from the  $K_xNa_{1-x}NbO_3$  perovskite phase in the same settings [47]. The dielectric permittivity decrease of the TTB phase from  $\epsilon_r \approx 200$  at low frequency to  $\epsilon_r \approx 130$  at high frequency is consistent with the decrease as reported in the literature. The loss tangent value  $\tan\delta$  at 10 GHz is about 20 % (Figure 11). The variation of  $\tan\delta$  from 1 to 5 GHz is attributed in part of the metal skin depth loss.  $\tan\delta$  at high frequencies remains much higher than 1.5 % measured at low frequency. The polyoriented growth of the TTB phase,

especially both in-plane and out-of-plane ordering of the nanorods, led to a quite rough film, and consequently to a rough metal-oxide film interface which may impact the loss.

The dielectric characteristics ( $\epsilon_r$  and  $\tan\delta$ ) at 10 GHz have shown no significant temperature dependence from 20°C to 240°C (Figure 11b). The variation of the permittivity and the slight increase in  $\tan\delta$  from 20% to 23% are attributed to the temperature increase of the device as a whole and of the measurement system. Therefore, the variations are not significant enough to hint a phase transition and are in agreement with the previous observations by Raman spectroscopy. The results also indicate a good stability of the dielectric characteristics at microwave frequencies in this range of temperature.



**Figure 11.** Variation of the dielectric characteristics (permittivity  $\epsilon_r$  and loss  $\tan\delta$ ) at high frequencies of the TTB thin film (F8) deposited on C-cut sapphire (a) depending on the frequency at room temperature and (b) depending on the temperature at 10 GHz.

The dielectric characteristics were also retrieved from the transmission lines under biasing ( $E_{bias}$  up to 27 kV/cm). No significant change was observed. Moreover the resonance frequency  $F_r$  of the CPW stub resonator printed on the KNN thin film was measured under various biasing to investigate a possible tunability (not shown here). A slightly open cycle shape has been evidenced, which could suggest a ferroelectric-like behavior. However the weak variation leading to a frequency tunability value lower than 1% could not be considered as a proof of a ferroelectric behavior.

## CONCLUSION

A tetragonal tungsten bronze structure in the K-Na-Nb-O system was successfully synthesized in thin films on various substrates using pulsed laser deposition technique. Thin films were deposited on both (100) and (110)SrTiO<sub>3</sub> with a highly oriented growth. Indeed dense microstructures with characteristic in-plane oriented nanorods were evidenced. Complementary characterizations (*i.e.* X-ray and electron diffraction, Raman spectroscopy) have also evidenced the TTB type phase growth. Piezoelectric Force Microscopy has shown an unambiguous piezoelectric local activity. However, high leakage currents made them impossible to switch the TTB polarization under an external DC electric field without destroying the sample.

Dielectric characteristics at room temperature were retrieved at low and high frequencies with a dielectric permittivity  $\epsilon_r \approx 200$  at 1 kHz and 130 at 10 GHz from thin films grown on (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si and C-plane sapphire substrates, respectively. The

electrical measurements, that were also restricted by high leakage current, have not shown ferroelectricity.

In order to perform further investigations on the physical behavior, it is essential to suppress the leakage current. For this purpose and to decrease loss, chemical doping could be envisaged as it has been performed in  $K_xNa_{1-x}NbO_3$  perovskite phase [48]. Indeed, the vacant crystallographic sites which characterize the TTB structure give a large possibility of improvement, modification and control of the TTB properties.

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**Highlights:**

- Pure tetragonal tungsten bronze phase films were grown by PLD in the KNN system
- The TTB structural features were shown by transmission electron microscopy and XRD
- Highly oriented thin films were grown on (100) and (110) SrTiO<sub>3</sub> substrates
- Dielectric characteristics were determined at low frequencies and in microwave
- High dielectric permittivity ( $\epsilon_r > 120$ ) was witnessed up to 40 GHz

Journal Pre-proof

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: