

Tunable TTB strontium and tantalum based thin films: influence of the deposition parameters on the structural and dielectric properties.

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Abstract

Structural and dielectric properties of thin films produced by reactive radiofrequency sputtering of a $(\text{Sr}_2\text{Ta}_2\text{O}_7)_{100-x}(\text{La}_2\text{Ti}_2\text{O}_7)_x$ target with $x = 1.65$ were studied. The chemical composition characterization shows Sr/Ta ratios ranging between 0.49 and 0.56, thus pointing out the deposition of strontium deficient films, belonging to the tetragonal tungsten bronze family. The highest permittivities and tunabilities, associated with the lowest dielectric losses, are obtained when films are pure and fully textured. This is achieved for a 900 nm-thick film deposited at $T_s = 850^\circ\text{C}$: $\epsilon' = 116$, $\tan\delta = 0.007$ and tunability $T = 14.5\%$ at 340 kV/cm and 100 kHz.

Key words : Perovskite phase; TTB phase; thin films; crystallization; dielectric characterization; tunability.

1. Introduction

The design of communicating objects constantly requires new technologies, in particular the development of devices operating on many frequency bands. This is currently achieved by using several antennas inside devices, which goes against the miniaturization of systems. To remedy this, two solutions are possible: either dedicate a specific antenna to each frequency and miniaturize it as best as possible, or, reduce the number of antennas by using only one antenna that can operate on several frequency bands, that is to say reconfigurable in frequency. This reconfigurability can be achieved using tunable electronic components or agile materials [1,2]. These ones can be used, either as a support for the radiating element, or integrated into localized components, for example capacitances. Ferroelectric materials are candidates of choice because their dielectric permittivity can vary under the action of an electric field. The use of these materials in the form of thin films then presents the advantage of being able to produce planar miniature devices, with low values of actuation.

Among the agile materials, the family of perovskite compounds is widely studied because of the flexibility of its crystalline structure and chemical composition leading to various electronic behaviors, from conducting compounds to semiconductors and insulators [3]. The study developed in this article concerns a new family of ferroelectric materials based on lead-free perovskites, having the formulation $(\text{Sr}_2\text{Ta}_2\text{O}_7)_{100-x}(\text{La}_2\text{Ti}_2\text{O}_7)_x$ (hereafter named as p-STLTO). $\text{Sr}_2\text{Ta}_2\text{O}_7$ (STO) and $\text{La}_2\text{Ti}_2\text{O}_7$ (LTO) are two ferroelectric perovskites, with Curie temperatures (T_C), respectively equal to -107°C [4] and to 1461°C [5], and they both belong to the layered-perovskite type of compounds [6]. This meets the requirement for the formation of a solid solution between STO and LTO, thus offering the possibility of controlling the properties of the synthesized STLTO materials, especially their permittivity and tunability. We have demonstrated the ferroelectric behavior of the p-STLTO family of compounds in the form of ceramics for $(\text{Sr}_2\text{Ta}_2\text{O}_7)_{100-x}(\text{La}_2\text{Ti}_2\text{O}_7)_x$ compositions with x ranging from 0 to 5 [7]. Optimal characteristics were achieved for $x = 1.65$: the permittivity value

was $\epsilon' = 375$ with a high tunability $T = 55\%$ at 30 kV/cm, 10 kHz and room temperature [8], associated to low dielectric losses $\tan\delta = 2 \cdot 10^{-3}$. Our work then focused on the transfer of the specific composition corresponding to $x = 1.65$ in the thin films form. A first study [9] was carried out on the deposition of oxide films by varying the percentage of reactive dioxygen during the deposition by magnetron Radio-Frequency (RF) sputtering starting from a p-STLTO target. Films were identified according to a new phase, not a perovskite one but a tetragonal tungsten bronze (TTB); the highest crystalline texturation of films was obtained for a percentage of 25% vol. of O_2 . The present study aims to study the effect of two others deposition parameters on the nature and dielectric properties of the deposited samples: the substrate temperature and the deposition time acting directly on the thickness of samples. As we will see below, all depositions lead, once again, to the formation of films with a TTB structure hereafter named as t-STLTO. Although not of a perovskite type, t-STLTO films present a tunability of their permittivity under electric field in low frequencies with the particularity of having very low losses and, thus, are of interest for integration in miniature frequency agile antennas.

The article is divided as follows: it first presents the experimental part, including the fabrication of the powdered target for sputtering, the deposition of thin films and the characterizations methods; then, it details the results concerning the two investigated series of deposited films and, finally, a conclusion and perspectives are given.

2. Materials and Methods

2.1. Target production for the sputtering deposition

The $(Sr_2Ta_2O_7)_{100-x}(La_2Ti_2O_7)_x$ powder with the composition $x = 1.65$, serving for the realization of the target for the sputtering deposition of films, has been synthesized using a standard solid-state process. Stoichiometric amounts of high purity powders of $SrCO_3$, Ta_2O_5 , La_2O_3 and TiO_2 were homogenized in isopropanol for 1 h in an agate mortar and dried in an oven at 110°C. The

obtained powder was pressed into a pellet using an uniaxial press, then calcinated in air for 15 h at 1000°C, milled and calcinated again at 1400°C for 15 h, and checked for phase identification by X-Ray Diffraction (Supplementary Data 1). The powdered product was clearly identified as an isotype of the Sr₂Ta₂O₇ perovskite compound (orthorhombic, S.G. = Cmcm) in agreement with the JCPDS 70-0248. Energy Dispersive Spectroscopy analysis of the powder gives strontium to tantalum ratio Sr/Ta = 1.00; lanthanum and titanium were observed in the spectrum but not quantified due to their low content (x = 1.65) in the synthesized (Sr₂Ta₂O₇)_{100-x}(La₂Ti₂O₇)_x compound.

Once the STLTO compound obtained as a powder, 74 grams were mixed to an organic binder (rhodoviol, 5 %wt.) to facilitate the shaping in a cylindrical pellet (diameter = 75 mm, height = 5 mm) and its maintenance to the deposition chamber. Compaction of the powder was made with an uniaxial press at 15 tons. Target was further heated at 600°C under air in order to eliminate the binder.

2.2. Thin film deposition

STLTO thin films were deposited by (Ar + O₂) reactive RF magnetron sputtering (Plassys MP450S) using the home made STLTO target located at 5 cm from the substrate holder. Reactive sputtering is used because, here, we want to produce oxide films: the addition of O₂ to argon during deposition helps in bringing oxygen and maintaining its level in the growing films. Magnetron sputtering is a conventional method of thin film deposition; magnetron helps to densify the electron presence near the target thus increasing its sputtering and, so, the deposition rate. This is especially important here because the used (oxide) target is sputtered with a high percentage of O₂, so in a poisoning process for which deposition rates are very low.

Before depositions, the chamber was pumped down to a base pressure of 10⁻⁵ Pa. During deposition, the dynamic pressure was maintained at 6 Pa (45 mTorr) with a percentage of dioxygen kept equal to vol.%O₂ = 25; this value corresponds to the optimum parameter determined in a

previous study [9]. RF power was fixed at $P_{RF} = 150$ W. Two kinds of deposition parameters were varied: the substrate temperature (T_S) from 700 to 900°C and the duration of the deposition acting directly on the thickness of films, the latter from 200 nm to 1500 nm.

At each run, films were deposited on two single-crystalline substrates obtained from Crystal GmbH (Berlin, Germany): MgO(001) and conductive niobium-doped (1.4 at.%) SrTiO₃(001) (Nb-STO). The latter has been used as substrate and bottom electrode for the dielectric characterization, while MgO is used to identify the phase in the XRD patterns. Indeed, because of a small crystallographic mismatch (+3.44%) between Nb-STO and Sr₂Ta₂O₇ (the prototype perovskite), the intense film's peaks of texturation are hidden by those of the substrate. The substrate MgO, which has a mismatch of -4.07%, also promotes a textured growth of films but substrate and films peaks can be easily differentiated.

2.3. Characterization methods

X-ray diffraction (XRD) patterns of films were obtained using a Rigaku SmartLab diffractometer (Cu K_{α1} radiation). Conventional Bragg-Brentano θ - 2θ and grazing in-plane 2θ - χ scans were recorded at 0.01° intervals with a 2 s count time at each step.

Cross-section morphologies for the determination of the thickness of films were characterized by Scanning Electronic Microscopy (SEM) using a Jeol JSM IT100 SEM. The error on the thickness values is estimated as being ± 20 nm. An example of a cross-section SEM micrograph for the thickness determination is given in Supplementary Data 2 for the STLTO-900nm-850C sample, that is for the film deposited at $T_S = 850^\circ\text{C}$ and having a thickness determined at 900 nm. Energy Dispersive Spectroscopy (EDS) was used to investigate the cations relative compositions of films; analyses were performed using the Aztek OXFORD software through the above SEM operating at 20 kV. An example of an EDS spectrum with the associated quantification is given in Supplementary

Data 3 for the sample SLTTO-900nm-850C; this film was deposited at $T_s = 850^\circ\text{C}$ and is thick enough (900 nm) so that there is no contribution of the atoms of the substrate.

Low frequency dielectric properties (permittivity ϵ' and dielectric losses $\tan\delta$) were measured by a LCR meter (LCR-819 GWInstek). Measurements were made on capacitance structures in which the bottom electrode is the Nb:STO substrate whereas 200 nm sputtered silver serves as the top electrode. Measurements were done from 1 kHz to 100 kHz at room temperature; external DC electric fields (0 – 30 kV) were applied at 100 kHz to point out a possible variation of the permittivity, i.e. a tunability (T) defined as $T(\%) = \frac{\epsilon'_{E} - \epsilon'_{E=0}}{\epsilon'_{E=0}}$.

AFM and PFM measurements were performed with a Park System NX10 equipment using a contact mode with a PtIr₅ coated pre-mounted PPP-EFM tip (Nanosensors) whose spring constant is ≈ 2.8 N/m. Off-resonance PFM signals were acquired simultaneously with AFM topography by means of a second internal lock-in. The driving voltage was set at 10 V at the probe tip and the conductive substrate was grounded.

Ferroelectric hysteresis P–E were characterized at room temperature ($f = 50$ Hz) using a Sawyer- Tower circuit with a 68 nF serial capacitor; a high voltage amplifier (Trek 609E-6, 0–2000 V) was used to tune the amplitude of the applied electric field.

3. Results and Discussion

3.1. t-SLTTO thin film deposition as a function of the substrate temperature

The first series concerns the deposition of STLTO films varying the substrate temperature (T_s) between 700°C and 900°C , for film thickness $t = 400$ nm. Samples are presented in Table 1.

Sample	T_s (°C)	%vol. O ₂	Thickness (nm)	Sr/Ta	Permittivity (ϵ')	Dielectric loss ($\tan\delta$)	Tunability(%) @200 kV/cm	Tunability max (%)
					100 kHz			
SLTTO-400nm-700C	700	25	400	0.50	25	0.004	0	0
SLTTO-400nm-750C	750			0.50	27	0.005	0	0
SLTTO-400nm-800C	800			0.53	29	0.003	0	0
SLTTO-400nm-825C	825			0.49	68	0.008	1.6	14.0 @810 kV/cm
SLTTO-400nm-850C	850			0.49	66	0.012	1.5	14.1 @810 kV/cm
SLTTO-400nm-900C	900			0.56	55	0.011	0.8	11.0 @810 kV/cm

Table 1. List of samples of the series "Substrate Temperature", along with some characteristics of STLTO films deposited by reactive magnetron sputtering.

Concerning the cation composition in films, the average atomic content of tantalum (~ 18 at.%) is in agreement with the theoretical value, but the percentage of strontium (~ 10 at.%) is much lower than the expected value. The Sr/Ta ratios are close to each other, in the range 0.49 – 0.56, as illustrated in Figure 1. The temperature of the substrate does not seem to affect the composition of the films; it seems therefore impossible to associate the strontium deficiency with a possible diffusion towards the substrate.

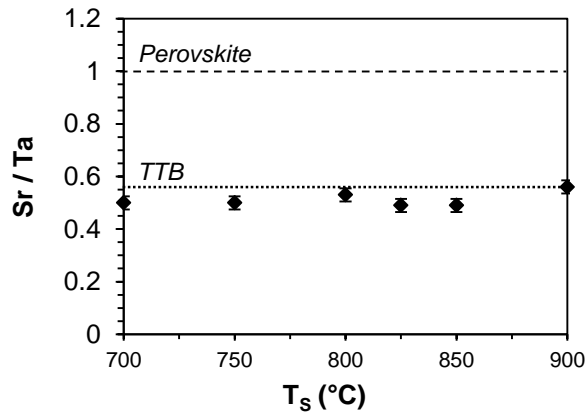
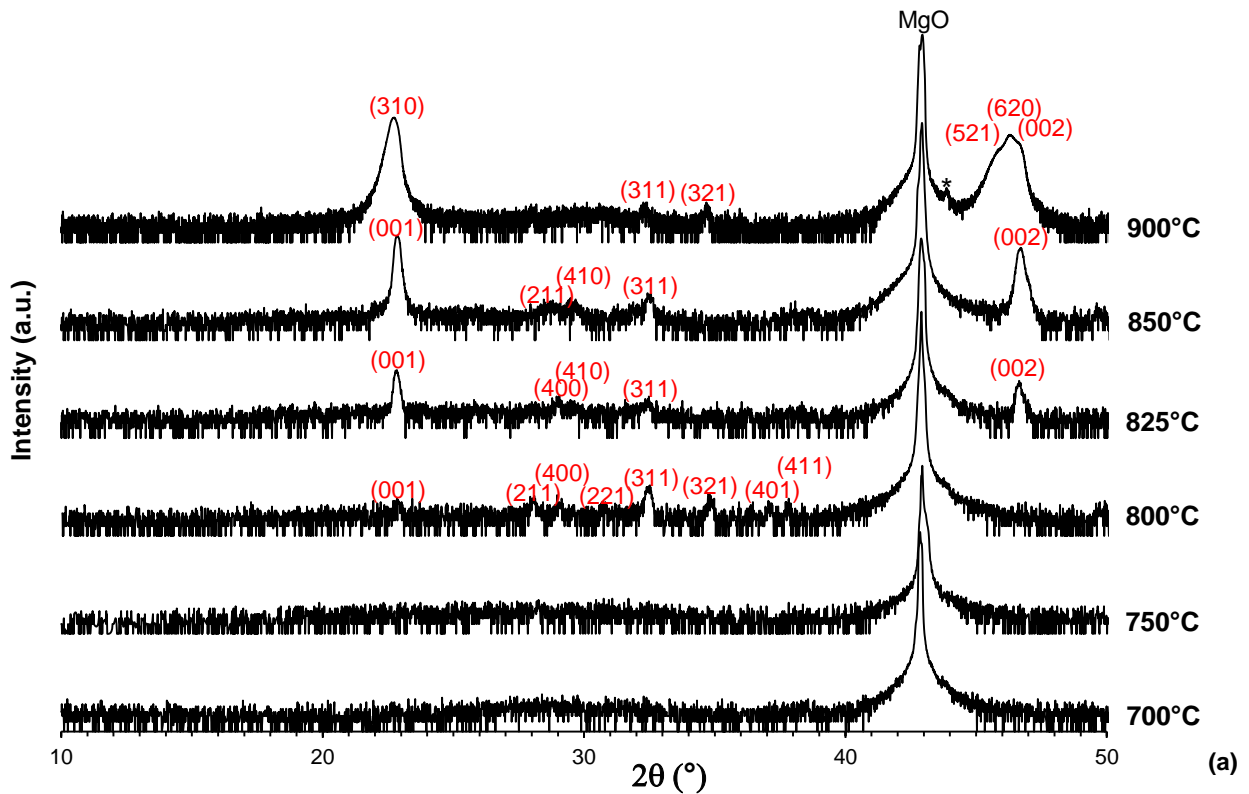


Figure . Evolution as a function of the substrate temperature (T_s) of the ratio Sr/Ta of t-STLTO thin films deposited on MgO substrates by reactive magnetron sputtering. Dotted lines at Sr/Ta = 1 and at Sr/Ta = 0.566 are drawn to mark, respectively, the Perovskite and TTB compositions.

XRD have been performed on the films deposited on MgO and Nb:SrTiO₃ substrates; patterns on MgO are shown in Figure 2a. The films deposited at temperatures $T_s \leq 750^\circ\text{C}$ do not

exhibit diffraction peaks apart from those of the substrate and can therefore be considered as amorphous. Peaks with low intensity belonging to the film compound appear at $T_S = 800^\circ\text{C}$; for $T_S \geq 825^\circ\text{C}$, some peaks are more intense than others, suggesting a textured growth. Let's focus on the SLTTO-400nm-800C sample, for which two complementary scans were performed (Figure 2b): the first one named "Bragg-Brentano" with a standard $\theta-2\theta$ configuration optimized on the film's peaks, and the second one named "Grazing in-plane" performed in grazing conditions ($2\theta = 0.5^\circ$ and $\omega = 0.5^\circ$) with a $2\theta-\chi$ scan in the plane of the sample available on the Rigaku Smartlab apparatus which provides a better film/substrate contrast. As can be seen in Figure 2b, these two scans together have enough peaks to perform accurate phase identification. At a first view, all film peaks seem to correspond to the targeted $\text{Sr}_2\text{Ta}_2\text{O}_7$ -type compound (ICD 00-030-1304), but, considering the ratio $\text{Sr}/\text{Ta} = 0.49 - 0.56$ of the SLTTO samples, compounds with a strontium deficiency have to be considered. The best indexation is made according to the $\text{Sr}_{2.83}\text{Ta}_5\text{O}_{15}$ material (PDF-9012069) having a ratio $\text{Sr}/\text{Ta} = 0.57$. In particular, contrary to the $\text{Sr}_2\text{Ta}_2\text{O}_7$ phase, this compound shows two peaks at $2\theta = 26.14^\circ$ and $2\theta = 35.09^\circ$ which fit well the peaks present in the SLTTO-400nm-800C film. One can however notice a slight angular shift of the 2θ positions of the film compared to those of $\text{Sr}_{2.83}\text{Ta}_5\text{O}_{15}$, arising because the latter does not contain lanthanum and titanium; this modifies the atomic positions, the reticular d_{hkl} distances and so the angular positions. $\text{Sr}_{2.83}\text{Ta}_5\text{O}_{15}$ has a tetragonal cell with $a = 12.2820 \text{ \AA}$, $c = 3.8640 \text{ \AA}$; it belongs to the family of tetragonal tungsten bronze (TTB) compounds. Finally, intense film peaks in Figure 2a are indexed as (001) and (002), which signifies a texturation of films along their c-axis, except for the film deposited at $T_S = 800^\circ\text{C}$ which is polycrystalline. The (00 ℓ) texturation increases with the deposition temperature but is never total in this series of samples, as evidenced by the polycrystalline contribution of the (311) peak always present for $T_S \geq 800^\circ\text{C}$. For $T_S = 900^\circ\text{C}$, a second texturation along the (310) family of planes is noticed, as well as a (521) contribution.

On Nb-STO substrates (Supplementary Data 4), film's peaks are present at $T_S = 825^\circ\text{C}$ and $T_S = 850^\circ\text{C}$ and correspond to a polycrystalline contribution. A (00 ℓ) texturation may also exist, hidden by the peaks of the Nb-STO substrate, since it was clearly evidenced for the films deposited on MgO substrates, as discussed above. At $T_S = 900^\circ\text{C}$, intense peaks appear close to those of Nb-STO substrate and may be related to a (310) or/and (001) texturation of the film.



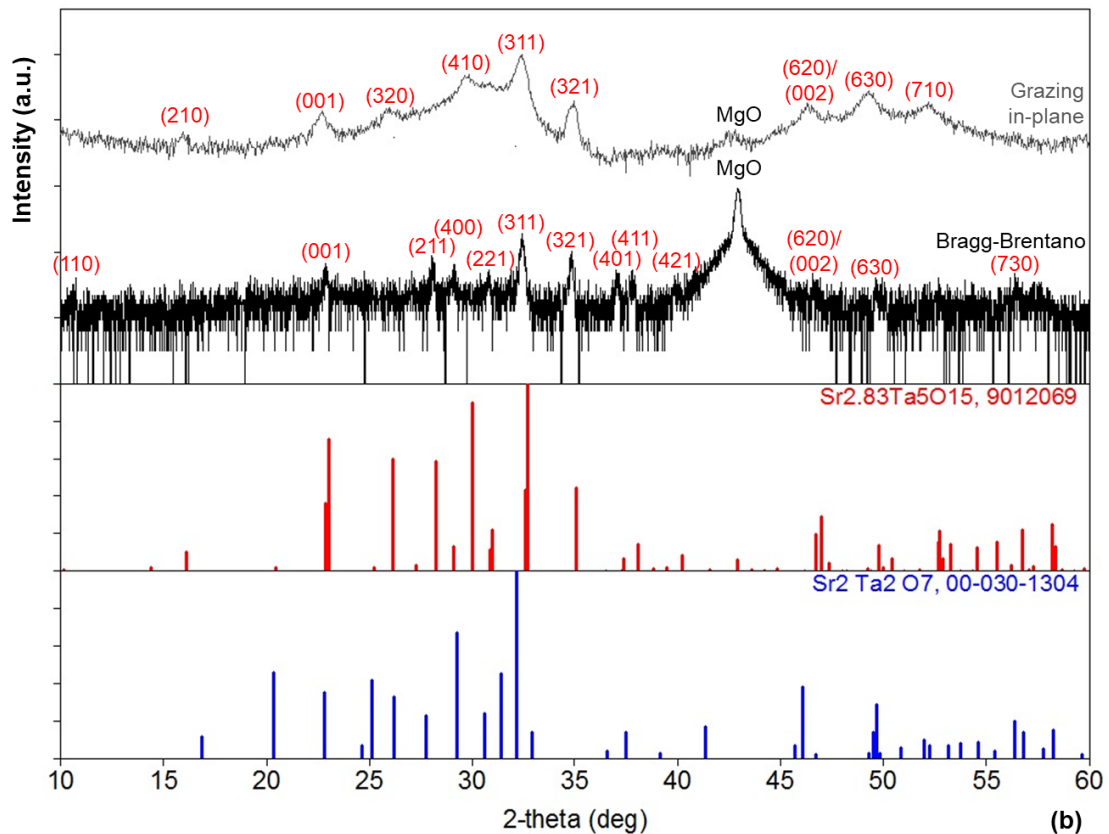


Figure 2. θ - 2θ XRD patterns of *t*-STLTO thin films with thickness of 400 nm deposited at different substrate temperatures (T_s) on MgO substrates by reactive magnetron sputtering: (a) full patterns and (b) Grazing in-plane and Bragg-Brentano scans of the film deposited at $T_s = 800^\circ\text{C}$ in comparison to the tabulated $\text{Sr}_{2.83}\text{Ta}_5\text{O}_{15}$ and $\text{Sr}_2\text{Ta}_2\text{O}_7$ phases. Indexation is made according to $\text{Sr}_{2.83}\text{Ta}_5\text{O}_{15}$ (*: sample holder).

Evolution of the permittivity (ϵ') and loss tangent ($\tan\delta$) of films deposited on Nb-STO substrate at different temperatures is presented in Figure 3. A bimodal distribution of the permittivity is noted: for $T_s \leq 800^\circ\text{C}$, the value of ϵ' is low around 30, whereas it rises at $\epsilon' = 68$ for $T_s = 825^\circ\text{C}$. In parallel, a jump of the loss tangent (from 4.10^{-3} to about 1.10^{-2}) is noticed. The abrupt change of the dielectric characteristics between $T_s = 800^\circ\text{C}$ and $T_s = 825^\circ\text{C}$ coincides with the beginning of the film crystallization on Nb-STO substrates; films thus exhibit high permittivity once they are crystallized. At $T_s = 850^\circ\text{C}$, $\epsilon' = 66$ and is very similar to the value obtained for $T_s = 825^\circ\text{C}$. These last two permittivity values are correlated to the same crystallinity, as seen in Supplementary Data 4: samples both exhibit a polycrystalline contribution with the appearance of the (311) peak; they can also be c-oriented with (001) peaks hidden by the substrate peaks). A low decrease of ϵ' is observed for $T_s = 900^\circ\text{C}$ with a value $\epsilon' = 55$. In XRD, this film does not exhibit a polycrystalline

contribution, as the previous ones, but two types of orientation, (310) and (001) in correlation with what is observed on MgO (Figure 2). This feature may account for its lower permittivity ($\epsilon' = 55$) compared to $\epsilon' = 68$ and $\epsilon' = 66$ obtained, respectively for $T_S = 825^\circ\text{C}$ and $T_S = 850^\circ\text{C}$.

Tunability of films follows the same evolution as a function of the deposition temperature than the permittivity: it become non-zero for $T_S \geq 825^\circ\text{C}$ as seen in Table 1. As illustration, Figure 4 shows the variation of the permittivity as a function of an electric field for the films deposited at $T_S = 800^\circ\text{C}$ (Figure 4.a) and $T_S = 850^\circ\text{C}$ (Figure 4.b): a variation is observed for the latter with a maximum tunability $T = 14.1\%$ at 810 kV/cm , with losses that remain low around $\tan\delta \sim 1.10^{-2}$ at 100 kHz .

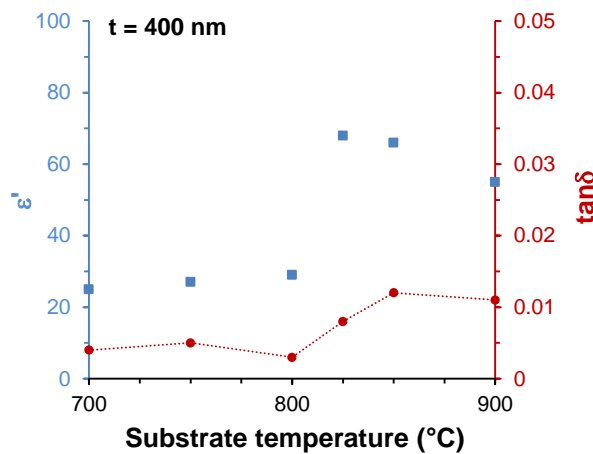


Figure 3. Evolution as the function of the substrate temperature (T_S) of the permittivity (ϵ') and the dielectric loss tangent ($\tan\delta$) of t -STLTO thin films with thickness $t = 400\text{ nm}$ deposited on Nb-SrTiO_3 substrates by reactive magnetron sputtering. Measurements made at 100 kHz and RT.

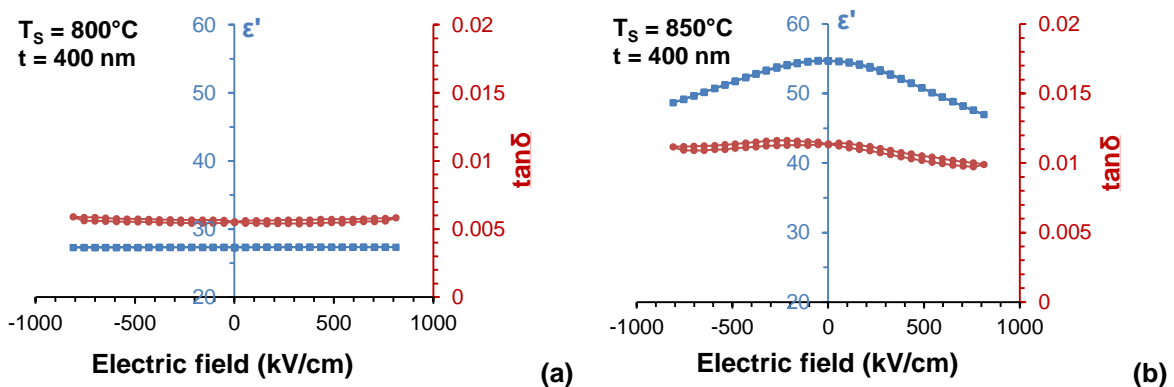


Figure 4. Evolution as the function of electric field of the permittivity (ϵ') and dielectric loss tangent ($\tan\delta$) at 100 kHz of t -STLTO thin films with thickness of 400 nm deposited on Nb-SrTiO_3 substrates by reactive magnetron sputtering at : (a) $T_S = 800^\circ\text{C}$ and (b) $T_S = 850^\circ\text{C}$. Measurements made at RT.

3.2. t-SLTTO thin film deposition as a function of the thickness of film

The second series of samples concerns films deposited keeping the substrate temperature constant at $T_s = 800^\circ\text{C}$ or $T_s = 850^\circ\text{C}$ while varying their thickness (t) from 200 to 1500 nm playing on the duration of the deposition (deposition rate is 2.97 nm/mn at $T_s = 800^\circ\text{C}$ and 2.67 nm/mn at $T_s = 850^\circ\text{C}$). The characteristics of the samples are summarized in Table 2.

Sample	Deposition duration (mn)	Thickness (nm)	T_s ($^\circ\text{C}$)	%vol. O_2	Sr/Ta	Permittivity (ϵ')	Dielectric loss ($\tan\delta$)	Tunability (%) @200 kV/cm	Tunability max (%)
SLTTO-400nm-800C	135	400	800	25	0.53	30	0.017	0	0
SLTTO-850nm-800C	287	850			0.49	93	0.014	2.2	5.8 @350 kV/cm
SLTTO-1500nm-800C	506	1500			0.52	116	0.002	5.0	5 @200 kV/cm
SLTTO-200nm-850C	75	200	850	25	0.56	65	0.020	3.5	9.9 @500 kV/cm
SLTTO-400nm-850C	150	400			0.49	66	0.012	2.1	14.1 @810 kV/cm
SLTTO-900nm-850C	338	900			0.52	128	0.007	7.0	14.5 @340 kV/cm
SLTTO-1150nm-850C	431	1150			0.50	109	0.022	5.5	8.4 @260 kV/cm
SLTTO-1400nm-850C	525	1400			0.52	82	0.005	3.2	3.5 @220 kV/cm

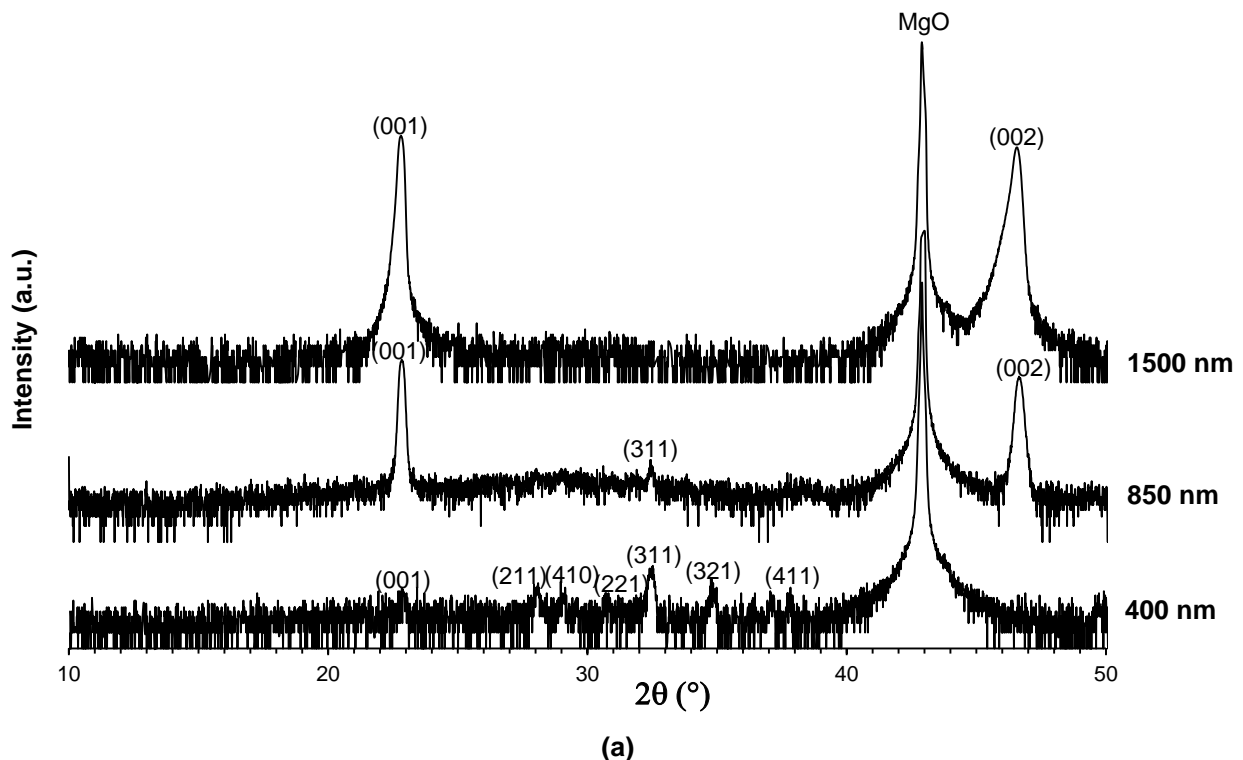
Table 2. List of samples of the series "Thickness", along with some characteristics of SLTTO films deposited by reactive magnetron sputtering.

The elemental analysis of the films points out Sr/Ta ratios between 0.49 and 0.56 for the two substrate temperatures; the thickness does not influence the chemical composition of the deposited films.

Figure 5 presents the XRD diagrams of films deposited on MgO substrates. For $T_s = 800^\circ\text{C}$ (Figure 5.a), all films are indexed according to the $\text{Sr}_{2.83}\text{Ta}_5\text{O}_{15}$ TTB phase. The 400 nm-thin film is weakly polycrystalline. The (00 ℓ) texturation increases with thickness; the 1500 nm-thick film is fully textured. For $T_s = 850^\circ\text{C}$ (Figure 5.b), films presents a (00 ℓ) texturation from the thickness of 200 nm; this texturation increases with temperature. However, all films exhibit a polycrystalline

contribution, except the 900 nm-thick film which is fully textured and has also the particularity of having a preferential (310) texturation. One can also observed the occurrence of another phase for the very thick films (1150 and 1400 nm) deposited at $T_s = 850^\circ\text{C}$, namely an isotype of the α - SrTa_2O_6 compound (orthorhombic, $a = 11.013 \text{ \AA}$, $b = 7.632 \text{ \AA}$, $c = 5.621 \text{ \AA}$, JCPDS 77-0943).

Concerning films deposited on Nb-STO (Supplementary Data 5), for $T_s = 800^\circ\text{C}$, no peaks are observed apart from those of the substrate for the film of thickness = 400 nm whereas the 850 nm-thick film is a mixture of the $\text{Sr}_{2.83}\text{Ta}_5\text{O}_{15}$ TTB and the α - SrTa_2O_6 phases with a strong polycrystalline character. The 1500 nm-thick film is fully (00 ℓ) textured according to the TTB phase. For $T_s = 850^\circ\text{C}$, the only (00 ℓ) fully textured sample is the 900 nm-thick film; a (310) texturation, clearly evidenced on MgO, may exist. The thinner and thicker samples present a polycrystalline contribution and the appearance of the α - SrTa_2O_6 phase for high thicknesses.



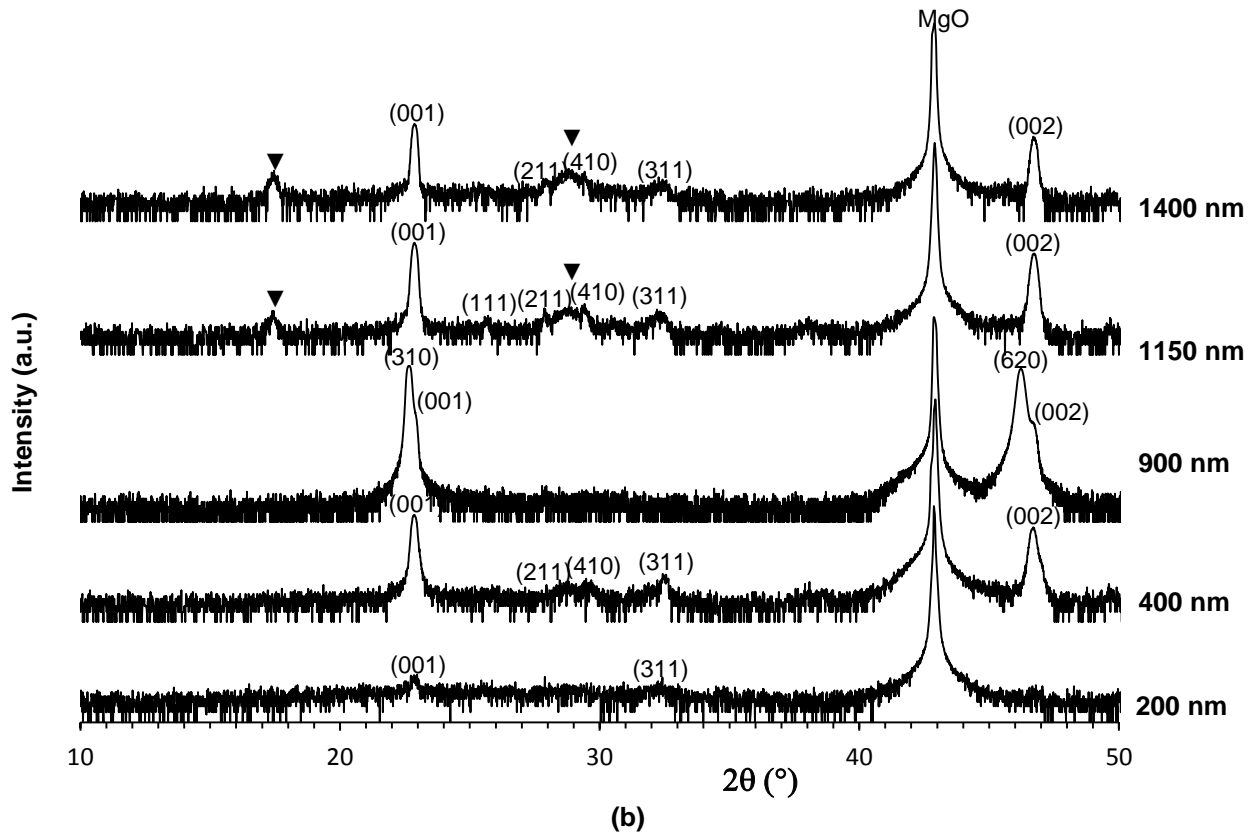


Figure 5. θ - 2θ XRD diagrams of *t*-STLTO thin films deposited at (a) $T_S = 800^\circ\text{C}$ and (b) 850°C with different thickness on MgO substrates by reactive magnetron sputtering (indexation according $\text{Sr}_{2.83}\text{Ta}_5\text{O}_{15}$; ▼: α - SrTa_2O_6). Thicknesses are indicated at the right of the curves.

Table 2 presents the values of permittivity and dielectric losses for the two sets of samples of the series as a function of the thickness. For $T_S = 800^\circ\text{C}$, a clear tendency is evidenced: permittivity and tunability increase and losses decrease when the thickness of films increases. This coincides with the greater (00 ℓ) texturation of films as thickness increases. The best characteristics are obtained for the 1500 nm-thick film: $\epsilon' = 116$, $\tan\delta = 0.002$ and $T_{(\text{max})} = 5\%$ at 200 kV/cm at 100 kHz (Figure 6a.). For $T_S = 850^\circ\text{C}$, such an evolution is not evidenced because a second phase appears for high thicknesses. The best characteristics (the highest of the study) are obtained for the film with thickness 900 nm: $T = 7\%$ @200 kV/cm and $T_{\text{max}} = 14.5\%$ at 340 kV/cm with $\tan\delta = 0.007$ and $\epsilon' = 128$ (100 kHz) (Figure 6b.). So, one can say that high dielectric performances are obtained when *t*-STLTO films are crystallized with a fully textured growth. As soon as the crystallization is low or a polycrystalline contribution or another phase exists, properties are degraded.

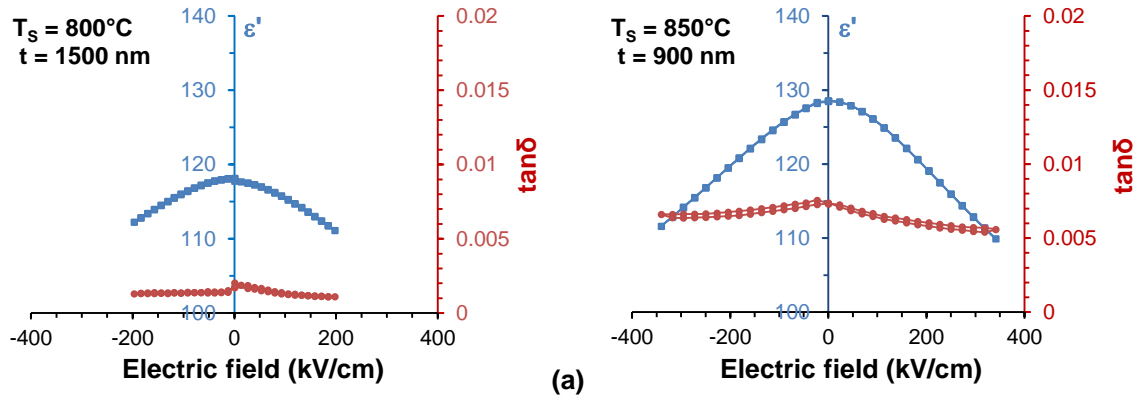


Figure 6. Evolution as the function of electric field of the permittivity (ϵ') and dielectric loss tangent ($\tan\delta$) at 100 kHz of *t*-STLTO thin films deposited on Nb-SrTiO₃ substrates by reactive magnetron sputtering at: (a) $T_s = 800^\circ\text{C}$ and (b) $T_s = 850^\circ\text{C}$. Measurements made at RT.

Complementary characterizations have been conducted on some samples deposited at $T_s = 850^\circ\text{C}$: AFM/PFM on the SLTTO-200nm-850C thin film (Figure 7) and P-E measurements on the SLTTO-400nm-850C and SLTTO-900nm-850C thick films (Figure 8). The height profile (Figure 7b) in the topographic AFM contrast (Figure 7a) reveals that the peak to valley roughness has a maximum value at around 7 nm. The PFM amplitude in Figure 7c. shows a significant piezoresponse in this 200 nm thin STLTO film, with minima attained in between grains. The phase of the piezo response in Figure 7d highlights a clear phase difference quantified at around 180° , which would mean an opposite out of plane polarization between scanned areas. These areas actually correspond to two types of grains as seen in the topographic PFM contrast in Figure 7e, with grains with a lamellar structure and other underlying grains. While this indicates the existence of active and inactive grains in the film, at this point of the characterization, the existence in the STLTO films of reversible ferroelectric domains, suggested by the phase contrast, is not fully demonstrated. At the same time, the P-E measurements (Figure 8) performed on 400 nm and 900 nm thick films do not show any macroscopic ferroelectric behavior. Indeed, the evolution of the polarization as a function of the electric field is linear for the 400 nm thick film, while it is open for the 900 nm film with a form evidencing electric losses rather than ferroelectric hysteresis. Considering the very low dielectric loss $\tan\delta$ values of the present films, one can explain the opening of the curve in the P-E response of the 900 nm thick STLTO film by the existence of defects in the material (oxygen

vacancies, interstitial atoms or ions,...) electroactive only at low frequencies (such as 50 Hz used in P-E measurements) and not at few tens of kHz. This is confirmed by the evolution at room temperature of the permittivity and dielectric loss of the STLTO-400nm-800C sample as a function of the frequency (Figure 9a): while the permittivity decreases very little, a sharp drop in losses from 1 kHz to 10 kHz is observed with $\tan\delta$ values decreasing from 0.096 to 0.018. This decay is the marker of electroactive defects in the sample causing a leakage current at very low frequencies. Meanwhile, the evolution of the permittivity and dielectric losses as a function of the temperature at 100 kHz (Figure 9b) of this sample does not evidence any variation of the permittivity in temperature; a slight increase of the losses is observed. No transition is thus pointed out on this film. At this point of our study, the ferroelectric character of the t-STLTO films is not evidenced

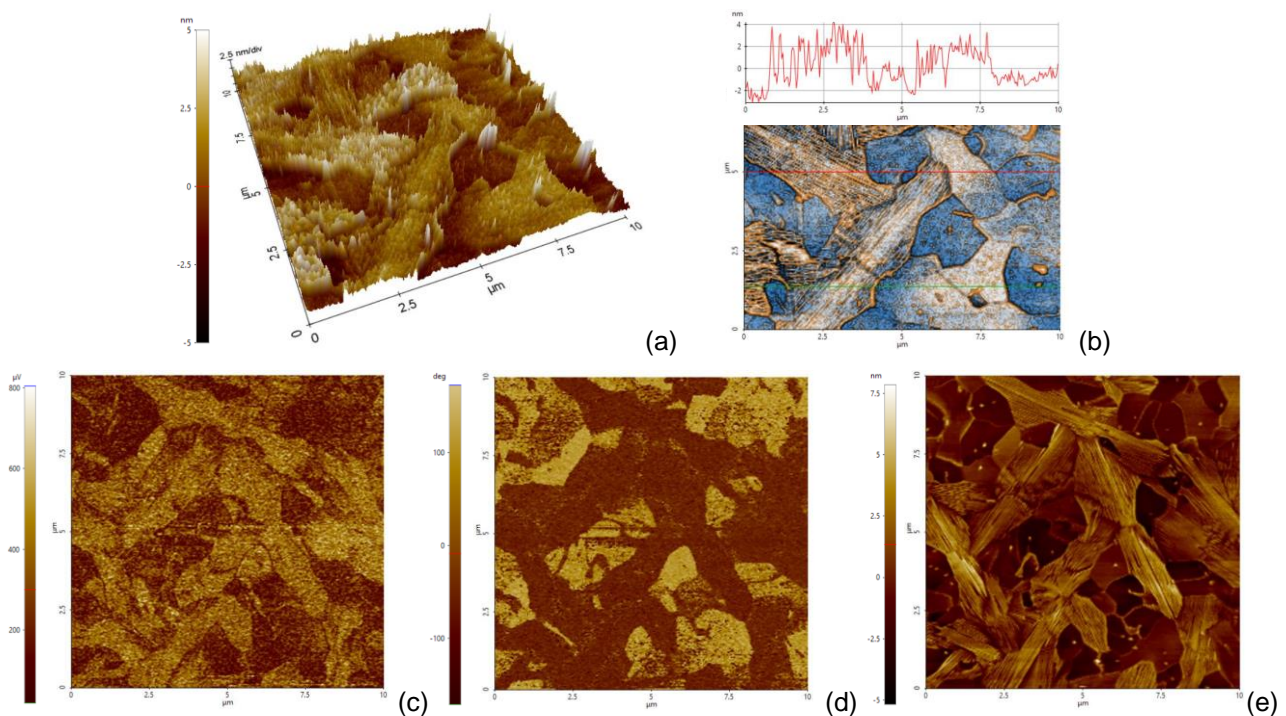


Figure 7. Atomic and Piezoresponse Force Microscopy signals of the STLTO film with thickness 200 nm deposited at $T_S = 850^\circ\text{C}$ on Nb-SrTiO₃ substrate by reactive magnetron sputtering: AFM (a) topography and (b) topography in enhanced color scale with line profile extracted along the red line, and PFM (c) amplitude (d) phase and (e) topographic signals.

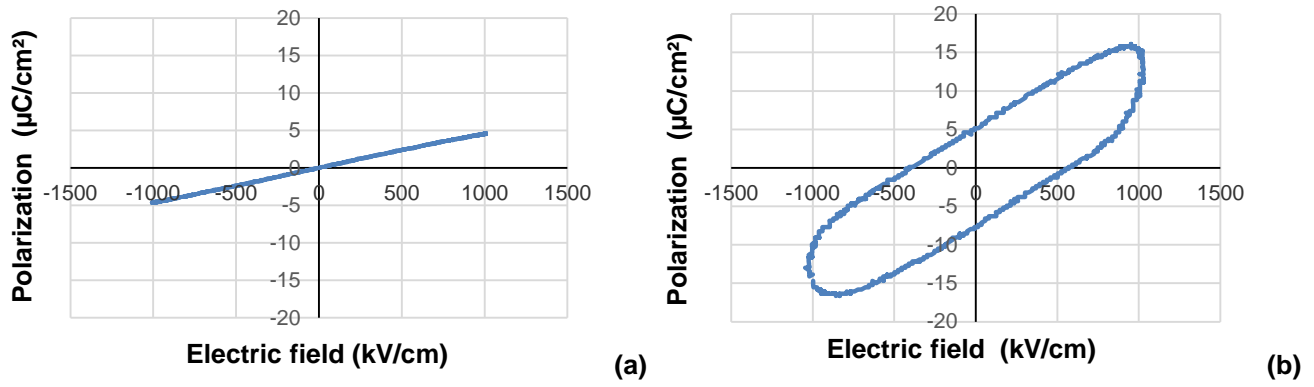


Figure 8. Polarization – Electric field (P - E) measurement ($f = 50$ Hz) performed at room temperature on t -STLTO films with different thickness: (a) 400 and (b) 900 nm, deposited at $T_s = 850^\circ\text{C}$ on Nb-SrTiO₃ substrates by reactive magnetron sputtering.

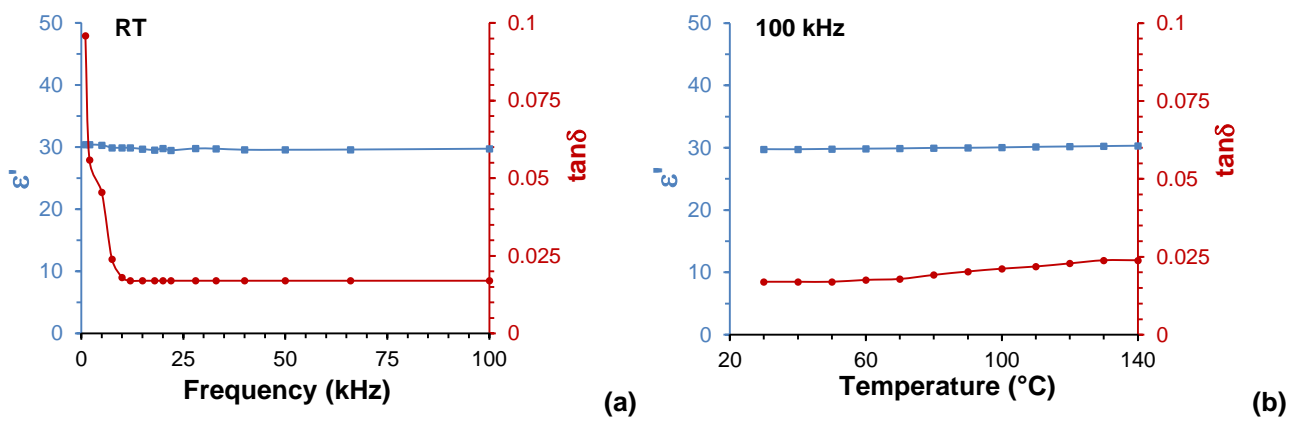


Figure 9. Evolution (a) as a function of the frequency at room temperature and (b) as a function of the temperature at 100 kHz of the permittivity (ϵ') and dielectric losses ($\tan\delta$) of the STLTO-400nm-800C thin film with thickness 400 nm deposited on Nb-SrTiO₃ substrate by reactive magnetron sputtering at $T_s = 800^\circ\text{C}$.

Films deposited during this study did not have the expected stoichiometric ($\text{Sr}/\text{Ta} = 1$) composition over the entire range of explored deposition parameters, i.e. substrate temperature and thickness, as well as percentage of reactive dioxygen as investigated in our previous study [9]. Films are indexed according to the TTB structure of the related Sr_{2.83}Ta₅O₁₅ compound. Despite this alternative composition, t -STLTO films show a tunability of their permittivity in the low frequencies, which meets, in part, our objective of synthesizing a new tunable compound. The present STLTO films do not offer large tunabilities as those obtained on standard ferroelectrics, for instance $T = 38.1\%$ at 150 kV/cm and 100 kHz ($\tan\delta \sim 0.03$) obtained on Ba_{1-x}Sr_xTiO₃ (BST) ($x = 0.4$) films in their paraelectric state at RT [10] or $T = 69.7\%$ at 400 kV/cm and 10 kHz ($\tan\delta = 0.03$) on (K,Na)NbO₃ (KNN) films [11]. But the undeniable advantage of the STLTO films lies in their very low dielectric

losses, here as low as $\tan\delta = 0.007$ with a permittivity $\epsilon' = 128$ and a tunability = 14.5 % at 340 kV/cm at 100 kHz (RT).

The $\text{Sr}_{2.83}\text{Ta}_5\text{O}_{15}$ compound with which we identify the STLTO films belongs to the family of the tetragonal tungsten bronzes. Like perovskites, this family of materials proceeds from the stacking of MO_6 octahedra, but the final structure is different: it reveals vacant volumes, or sites, which may be unoccupied or filled with cations whose size will be in relation to the available volume [12,13]. The compounds we have studied mainly contain Sr^{2+} and Ta^{5+} cations, and La^{3+} and Ti^{4+} cations as dopants. In the TTB structure, the Sr^{2+} can be positioned in sites A and B, of respective coordination 15 and 12, the La^{3+} in A sites and the Ta^{5+} and Ti^{4+} will constitute the M metal ions of the structure. It is also possible for the Sr^{2+} to be positioned at M sites, as was suggested by M.R. Brophy *et al.* in their study of the annealing in air of SrTaO_2N films [14]. TTBs containing simultaneously the four cations Sr^{2+} , Ta^{5+} , La^{3+} and Ti^{4+} have not been reported in the literature. TTBs containing some of these ions have been studied: for instance, $\text{Sr}_5\text{RTi}_3\text{Ta}_7\text{O}_{30}$ (R = Sm, Y) [15] in the form of ceramics with permittivities around 110 and losses of the order of $4 \cdot 10^{-3}$ at 1 MHz, and $\text{Sr}_4\text{La}_2\text{Ti}_4\text{Nb}_6\text{O}_{30}$ [16] ceramics, with permittivities around 500, with losses lower than $8 \cdot 10^{-3}$ at 1 MHz. No tunability has been reported for these ceramic compounds, but a diffuse ferroelectric phase transition was observed around -30 °C for $\text{Sr}_4\text{La}_2\text{Ti}_4\text{Nb}_6\text{O}_{30}$, with a disordered distribution of Ti^{4+} and Nb^{5+} in B sites, confirmed by XRD refinement; this could be the origin of a relaxor ferroelectricity. As thin films, a tunability is reported for $\text{Ba}_6\text{Ti}_2(\text{Nb}_{0.6}\text{Ta}_{0.4})_8\text{O}_{30}$ (doped BTN) TTB samples deposited by PLD [17]: tunability is lower than 10 % with loss $\tan\delta \sim 0.025$; this composition is quite far from ours. Finally, the behavior of the t-STLTO films turns out to be closer to that of oxides containing only strontium and tantalum, i.e. SrTa_2O_6 type. We can cite the work of Kim *et al.* [18] on the TTB β' - SrTa_2O_6 compound: the permittivity of ceramics is 110, close to our values; the ferroelectric character has not been tested. As thin films, Regnery *et al.* [19] described the MOCVD deposition and post-annealing at 800°C of Sr-Ta-O films whose Sr/Ta ratio varies from 0.40 to 1.48. Films with $\text{Sr}/\text{Ta} \geq 0.80$

present the XRD signature of the perovskite $\text{Sr}_2\text{Ta}_2\text{O}_7$; permittivities are low ($\epsilon' = 40$), as are the dielectric losses ($\tan\delta = 3.10^{-3}$) (RT, 100 kHz). Films with ratios $0.40 \leq \text{Sr}/\text{Ta} \leq 0.60$ are identified as TTb with permittivities $\epsilon' = 100 - 110$ and $\tan\delta \sim 0.1$ (100 kHz). The slightly higher values of the current best t-STLTO sample ($\epsilon' = 128$, $\tan\delta = 0.007$) may result from the quality of the textured growth of this sample, because, as demonstrated once again here, dielectric characteristics of films strongly depend on their structural characteristics resulting from the deposition conditions. It can also arise from the intrinsic effect of the addition of La and Ti, because the diversity of ions in the STLTO compounds pleads in favor of a cationic disorder effect specific to TTbs, thus leading to even more exacerbated dielectric characteristics while keeping low dielectric losses.

4. Conclusion

Chemical, structural and dielectric characterization of STLTO thin films deposited by radio-frequency sputtering from a $(\text{Sr}_2\text{Ta}_2\text{O}_7)_{0.9835}(\text{La}_2\text{Ti}_2\text{O}_7)_{0.0165}$ target was conducted. The impact of the substrate temperature and the deposition time (so, thickness) on the film characteristics was probed. EDS chemical composition analysis points out Sr/Ta ratios in the range 0.49 - 0.56. These values do not correspond to the targeted perovskite $(\text{Sr}_2\text{Ta}_2\text{O}_7)_{0.9835}(\text{La}_2\text{Ti}_2\text{O}_7)_{0.0165}$ compound with a Sr/Ta ratio = 1. The XRD analysis identifies films to a compound isotype to $\text{Sr}_{2.83}\text{Ta}_5\text{O}_{15}$, belonging to the family of tetragonal tungsten bronzes.

The temperature series of samples, carried out from 700 to 900°C, evidences a minimum temperature of $T_s = 800^\circ\text{C}$ for the crystallization of 400 nm-thin films. Films present a textured growth along their c-axis, increasing with T_s . Crystallized films have higher permittivities ($\epsilon' = 55 - 68$) than amorphous samples ($\epsilon' \approx 30$). The series with variation of film's thickness points out that this parameter is not the pertinent one: the highest permittivities and tunabilities, as well as the lowest dielectric losses, are obtained from the moment that films are fully textured. This is achieved for a 1500 nm-thick film deposited at $T_s = 800^\circ\text{C}$, and for a 900 nm-thick film deposited at $T_s =$

850°C, with, for this sample, the highest performances of the study: tunability $T = 14.5\%$ at 340 kV/cm and dielectric losses $\tan\delta = 7.10^{-3}$ (100 kHz, RT). At $T_S = 850^\circ\text{C}$, greater thicknesses result in the appearance of a second phase isotype to the $\alpha\text{-SrTa}_2\text{O}_6$ orthorhombic compound and the dielectric characteristics are degraded. Future work will focus on the high frequency dielectric characterization of the STLTO films, with the aim to integrate them in frequency agile devices such as planar miniature and agile antennas.

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