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► **To cite this version:**

M. Jędrusik, Ch. Turquat, P. Eyméoud, A. Merlen, Madjid Arab, et al.. LaFeO₃ thin films on Yttria Stabilized Zirconia flexible substrate. *Thin Solid Films*, 2023, 780, pp.139951. 10.1016/j.tsf.2023.139951 . hal-04290861

HAL Id: hal-04290861

<https://hal.science/hal-04290861v1>

Submitted on 19 Jul 2024

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LaFeO₃ thin films on YSZ flexible substrate

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Highlights :

- LaFeO₃ thin films were successfully grown on tetragonal flexible YSZ substrate for the first time
- The occurrence of vacancies in LaFeO₃ thin films was evidenced through Raman spectroscopy, as well as Chemi-Stem.
- LaFeO₃ thin films has two types of grain termination, flat or tip-like
- {112} twins in LaFeO₃ were observed as a consequence of the grain curvature of T-YSZ substrate.

Abstract :

Thin films of LaFeO₃ were grown by pulsed laser deposition on a flexible tetragonal yttria stabilized zirconia substrate. Their structure and morphology were investigated using SEM, TEM, Chemi-STEM EDS, XRD and Raman Spectroscopy techniques. All grains of the polycrystalline substrate T-YSZ were covered by a homogeneous LaFeO₃ film, even at the grain boundaries. The thin films are 100 nm thick with nanocrystalline grains around 60 nm in lateral size. The chemical analyses show deficiency of Fe in the thin film. Atomic-scale microstructure investigations revealed twins in LaFeO₃ grains, as adaptation to the curvature of the T-YSZ grains. The main growth directions of the grains are [110] and [010]. Flat ended

and tip-like grains were observed, as in LaFeO₃ thin films deposited on silicon. The exposed facets are {110} or {010} for flat ended grains, {010} and {100} for tip-like termination.

This work shows the feasibility of covering flexible T-YSZ substrate with homogeneous perovskites thin films by PLD, that may be used for flexible sensing devices.

Keywords: LaFeO₃, thin films, PLD, T-YSZ substrate

1. Introduction

The LaFeO₃ orthoferrite compound has been already reported for various applications, such as gas sensing, catalysis, photocatalysis, and solid oxides fuel cells. LaFeO₃ is a mixed ionic and electronic conductor (MIEC), is one of the most promising catalytic material for the production of hydrogen, by reduction of CO₂ [1], CH₄ [2], or by water splitting [3]. Due to a band gap of 2.6 eV, corresponding to a wavelength of 475 nm (blue light), the photocatalytic activity of LaFeO₃ under visible light was demonstrated, in case of degradation of organic pollutant [4], but also on the photoelectrochemical water splitting [5,6]. LaFeO₃ films were efficient in the detection of NO₂, as sensing electrodes in electrochemical gas sensors [7] or in semi conducting metal oxide-based gas sensors [8]. Thick films of LaFeO₃ proved to be selective to acetylene in a gas mixture containing also CO, H₂, and CO₂ [9]. Detection of formaldehyde at the ppb level could be realized with thin films of LaFeO₃ [10]. In recent works, depending on the application field, and the expected microstructure, several substrates on which the films are deposited were used. Epitaxial thin films were grown on SrTiO₃ [11], MgO [12], or GdScO₃ [13], when control of the interfaces or twin free films were needed. When seeking integration on micro electronic devices, LaFeO₃ thin films were grown on silicon [14, 15]. For devices implying charge carriers exchange between substrate and film, like in solid fuel cells or electrochemical sensors, yttria-stabilized zirconia (YSZ) is often used as substrate, because of its high ionic conductivity and low electronic conductivity at high temperature combined with chemical and crystallographic inertness over a wide range of temperature [16-18]. All these substrates are rigid, but it could be interesting to grow LaFeO₃ on flexible substrates. Indeed, there is a growing need of flexible sensing devices, able to adapt to various shapes, for applications that requires bending, or folding of the material [19]. Flexible layer of polymer composite with LaFeO₃ nanoparticles with high permittivity and low dielectric loss were recently elaborated [20]. Strain engineering leads to new properties for thin films grown on flexible substrates, as was recently demonstrated by Wu *et al.* in 2021 [21], in the case of flexoelectric LaFeO₃ photodetectors.

In this work, we selected tetragonal yttria stabilized zirconia (T-YSZ) as flexible substrate and used Pulsed Laser Deposition to grow thin films of LaFeO_3 on it. This is the first time in literature that T-YSZ is reported as substrate for the direct growth of thin oxide films. Up to now, T-YSZ was barely used in literature as substrate for thick oxide films [22] or buffer layer for the growth of ZnO thin films on silicon [23]. Only recently, ultra-thin (20 μm) T-YSZ flexible substrates were investigated for infrared nano optics [24], T-YSZ tapes for their mechanical properties [25] and for their thermal conductivity [26]. T-YSZ was also used in SOFC instead of C-YSZ to improve the mechanical strength of the NiO-YSZ anode [27]. Two dimensional MoS_2 semi-conductors were recently grown on T-YSZ covered by 50 nm of SiO_2 [28].

The structure and microstructure of the LaFeO_3 thin film on T-YSZ was fully characterized by means of X rays diffraction and various electron microscopies (SEM, TEM and STEM-HAADF). Information about the stoichiometry of the films was obtained by local and line scan EDS analyses, as well as Raman spectroscopy.

2. Experimental procedure

3T-YSZ (3 %wt. Y_2O_3) substrates 100 mm x 100 mm x 0,1 mm were purchased from Zircar Zirconia Inc. These sheets have a bending strength of 1 GPa. The corresponding radius of maximal curvature in case of pure bending can be calculated, considering a Young's modulus of 200 Gpa for 3T-YSZ [25]. For a thickness of 100 μm , the bending radius is about 10 mm. The LaFeO_3 thin films were deposited by Pulsed Laser Deposition using a Nd-YAG laser ($\lambda=266\text{nm}$), the LaFeO_3 target being purchased from Kurt Lesker Company. The deposition conditions were an oxygen pressure of 5,3 Pa (40 mTorr), an energy of laser of 90 mJ, a pulse frequency of 10 Hz, a duration of 4 ns, and a deposition time of 150 min. The distance between the target and the substrate was fixed at 70 mm. Two deposition temperatures, 750 °C and 850°C were used, but only the latter temperature led to crystallized LaFeO_3 . Consequently, the results presented in this paper will focus on films deposited at 850°C.

The X-rays diffraction patterns were collected in grazing incidence ($\lambda=1^\circ$) using a PANalytical EMPYREAN DY 1061 with a Cu $K\alpha$ tube. Cell parameters were refined using the software Maud. The topography of the films was observed using a Scanning Electron Microscope Zeiss Supra 40, with an Inlens detector.

The samples for transmission electron microscopy (TEM) were prepared using a FIB ZEISS NEON 40EsB CrossBeam microscope. Conventional Transmission Electron Microscopy was performed on a TecnaiG2 ST equipped with a Si (Li) EDAX detector for X-Energy Dispersive Spectroscopy (EDS). More than 20 EDS local chemical analyses were acquired along the cross section of the layer, and the K factors for quantification of La and Fe were determined using the LaFeO_3 target as standard. High resolution High Angle Annular Dark Field (HAADF)

images were acquired on a Titan cube G2, Cs corrected, operated at 300 kV, equipped with a Chemi STEM EDS system, allowing chemical elements line scans or mapping. Line scans with a step of one nm were realized from the substrate to the top of the layer, along the growth direction of the LaFeO_3 grains, and parallel to the substrate, near the free surface and near the substrate, in order to gain information on the homogeneity of the LaFeO_3 film.

The chemical composition was also investigated by Raman spectroscopy using a Horiba-Jobin-Yvon HR LabRAM HR800 Raman spectrometer, with two Ar ion laser wavelengths (488nm and 514nm). The acquisition parameters were a x50 long-working distance objective, 50% of 2mW laser power and an acquisition time of 5 minutes. The theoretical spatial resolution by $R = 0.6 \cdot \lambda / NA$ (with $NA=0.5$ and λ the used wavelength), and the spectral resolution is about 1 cm^{-1} .

3. Results and discussion

3.1 Microstructure

The topography of LaFeO_3 -850/T-YSZ thin film was investigated by SEM (Fig.1). The T-YSZ substrate presents a bumpy polycrystalline surface. Grains are ranging from 0.2 to 1 μm in sizes and present smooth rounded terminations. The grains boundaries are clearly visible grain boundaries. After PLD deposition, SEM observations showed that the LaFeO_3 layer covers the substrate without discontinuity — grains and grain boundaries alike — and follows the substrate texture. The presence of irregular droplets of LaFeO_3 on the surface of the film (example encircled in Fig. 1) are well-known PLD artifacts and will not be discussed furthermore.

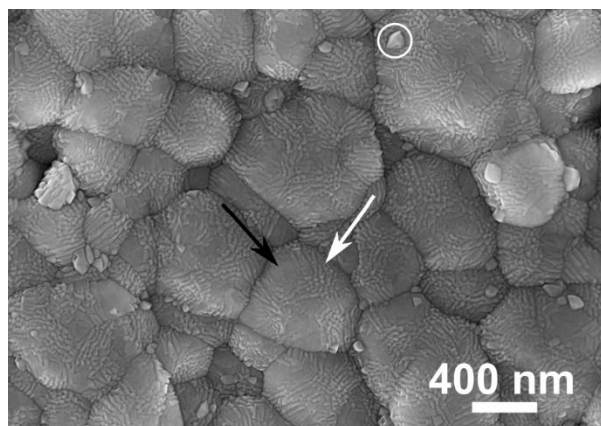


Figure 1. Topographic SEM image (SE) of LaFeO_3 -850/T-YSZ. Arrows show the two typical types of surface texture present in the image. Encircled area shows a droplet i.e. a typical PLD artifacts.

The LaFeO_3 film presents a similar nanostructure than the one observed in previous work [14], with two distinctive areas. One area displays a rather smooth surface (black arrow on Fig. 1) that from experience can be associated with LaFeO_3 grains with flat terminations. The

observation of the other area (white arrow on Fig. 1) shows a rougher surface with one privileged growth route, suggesting a compact juxtaposition of wall-like grains with pointy top terminations. It is interesting to note that the wall-like structures seem to be wrapped around the smooth areas. The shape of the smooth areas is not well defined although their analysis via the DigitalMicrograph software shows that in average the smooth areas present a major axis 37% longer than its minor axis; there is no preferential direction for major axis. The smooth areas cover 9% of the image which is significantly larger than the 6% we observed in a previous work [14]. Besides, our early work suggests that the proportion of smooth area is temperature dependent; the higher the temperature, the lower its proportion is. Hence, this discrepancy could be attributed to the much lower thermal conductivity of the T-YSZ substrate as compared to the thermal conductivity of silicon that was used as substrate in our early work, resulting in a lower effective surface temperature in the case of T-YSZ substrate. Indeed, the value of thermal conductivities for dense substrates at $T=800\text{ }^{\circ}\text{C}$ are respectively $\kappa=2,5-3\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for T-YSZ and $\kappa=30-40\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for Si single crystal [29,30].

The TEM cross sectional view in Fig. 2 shows a complete covering of the polycrystalline T-YSZ substrate, despite its bumpy nature. The LaFeO_3 layer is 100 nm thick, with columnar grains starting from the substrate.

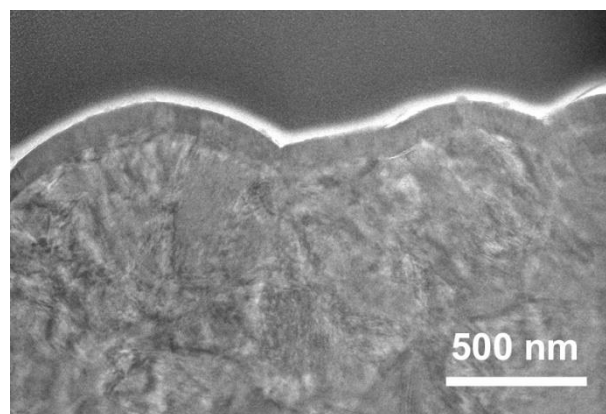


Figure 2. Cross sectional TEM view of a LaFeO_3 -850/T-YSZ sample prepared by FIB.

3.2 Crystallographic structure

The LaFeO_3 crystallographic structure is an orthorhombic deformation of the well-known cubic perovskite cell, linked to the tilting of FeO_6 octahedra around the axes of the cubic cell and leading to a doubling of the cell parameter along one axis. Two settings are used in literature to describe the orthorhombic space group n° 62 of LaFeO_3 , namely $Pbnm$ and $Pnma$. We choose the former, for which the c-axis is the long axis of the unit cell. The experimental XDR pattern of the LaFeO_3 thin film is shown in Fig. 3 (blue line), along with the calculated one

from refinement procedure (red line) and the difference between experimental and calculated pattern (green line). Peaks from the substrate are present along with the peaks for the LaFeO₃ phase. This indicates that the film thickness is smaller than the penetration depth of X rays in the case of grazing incidence with $\alpha = 1^\circ$ around 90 nm [14]. Refinements of the cell parameters, crystallite size and strain and cation positions were pursued in the case of a two-phase system, the orthorhombic phase of LaFeO₃ (CIF file n° 1526450) and the tetragonal YSZ (CIF file n° 1521474). The background was fitted with a 5th order polynomial function and the peaks with pseudo-Voigt functions. Errors on cell parameters are $2 \cdot 10^{-3}$ Å. The crystallite size is given with an error of 5 nm and strain with an error of $2 \cdot 10^{-4}$. The results concerning the LaFeO₃ phase are reported in Table 1 and 2.

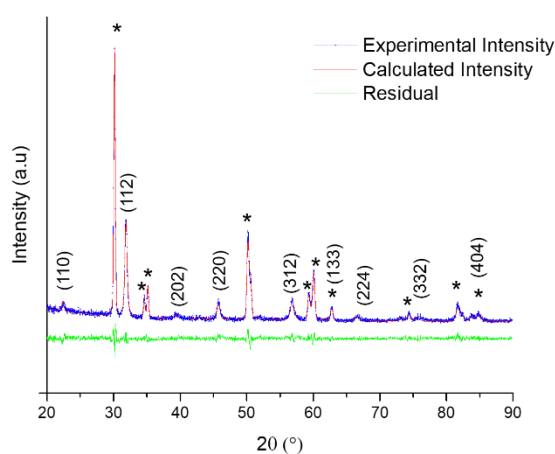


Figure 3. Experimental X-rays pattern of LaFeO₃ grown by PLD at 850°C on T-YSZ, along with the calculated pattern from Rietveld refinements and the difference between both diagrams. Peaks with an asterisk (*) originate from the substrate.

Table 1.

Cell parameters, volume cell, crystallite size and refinement R factors on LaFeO₃ grown on T-YSZ, compared to results obtained for films grown on Si [14].

Sample	a (Å)	b (Å)	c (Å)	V (Å ³)	Size (nm)	Strain	R _{exp} / R _{wp}
LaFeO ₃ -850/T-YSZ	5.572	5.623	7.958	249.35	58	0.0025	11.4/14.3
LaFeO ₃ -850/Si	5.539	5.613	7.912	245.99	52	0.0024	8.4/11.2
LaFeO ₃ -750/Si	5.573	5.609	7.951	248.51	57	0.0022	11.1/13.1

Cell parameters, crystallite size and strain are much alike those obtained under the same deposition conditions on a silicon [100] substrate at a deposition temperature of 750°C instead of 850°C [14]. This can be linked to the much weaker thermal conductivity (k) of T-YSZ compared to Si [29,30]. It shows also that the thermal conductivity of substrate may influence

the cell parameters of thin films grown by PLD. Concerning the refined atomic positions (Table 2), let us recall that the orthorhombic perovskite structure of LaFeO_3 (space group n°62) is built by the piling up of corner-linked FeO_6 octahedra, tilted in opposite directions. The four oxygens noted O_2 lay in the equatorial plane of the FeO_6 octahedra as the two oxygens noted O_1 correspond to the apex of the octahedron. As for the La cation, they occupy a body centered position with regards to the surrounding Fe cations and are coordinated to 12 oxygens (four O_1 and eight O_2). The refined atomic positions, obtained with an error of 10^{-2} on oxygen positions and 10^{-3} on La positions, are near those obtained for LaFeO_3 grown on Si at 750°C , but differs from those given in [31, CIF file n° 1526450]. Fe-O bond lengths and O-Fe-O bond angles are a signature of the deformation of the FeO_6 octahedra in the perovskite structure, so they were reported in Table 3.

Table 2

Refined atomic positions for LaFeO_3 -850/T-YSZ compared to refined atomic positions obtained in literature.

	LaFeO₃-850/T-YSZ			LaFeO₃-750/Si [14]			CIF n° 1526450 [31]		
	x	y	z	x	y	z	x	y	z
Fe	0	0.5	0	0	0.5	0	0	0.5	0
La	0.999	0.012	0.25	0.002	0.022	0.25	0.993	0.0297	0.25
O ₁	0.057	0.445	0.25	0.061	0.467	0.25	0.080	0.485	0.25
O ₂	0.792	0.357	0.001	0.818	0.296	0.969	0.719	0.302	0.029

Table 3.

Bond lengths and bond angles for LaFeO_3 -850/T-YSZ compared to data from literature.

Sample	LaFeO₃-850/T-YSZ	LaFeO₃-750/Si [14]	CIF n° 1526450
Fe-O₂ (Å)	2.584	2.442	2.0863
	2.584	2.442	2.0863
	1.410	1.548	1.9232
	1.410	1.548	1.9232
Fe-O₁ (Å)	2.039	2.025	2.0121
	2.039	2.025	2.0121
O₁-Fe-O₂ (°)	77.7	73.46	86.80
	92.1	78.43	87.70
O₂-Fe-O₂ (°)	85.7	89.3	88.60
	94.3	90.63	91.40

The deformation of the FeO_6 octahedra in LaFeO_3 -850/T-YSZ occurs mainly in the equatorial plane, as it is the case in LaFeO_3 -750/Si. From the angle values, one can conclude that Fe cations are not at the center of octahedra equatorial planes. The distorted FeO_6 octahedra deduced from Rietveld refinement of XRD patterns were drawn Fig. 4 for clarity.

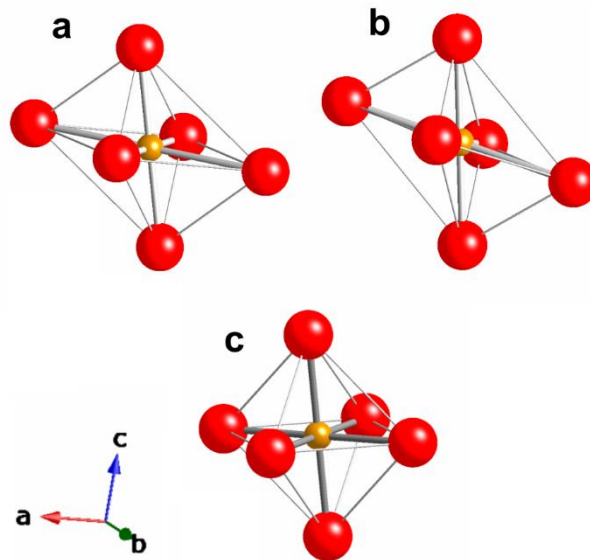


Figure 4. FeO_6 octahedra deduced from Rietveld refinement, in case of LaFeO_3 -850/T-YSZ, LaFeO_3 -750/Si, and LaFeO_3 [31, CIF file n° 1526450]

3.3 Chemical composition

The chemical composition of the LaFeO_3 -850/T-YSZ thin film was investigated using different spectroscopies. Local EDS analyses (see Fig. 5a for a characteristic spectrum showing the peaks characteristic of La, Fe, as well as the Cu peaks due to TEM copper grid used) gave a mean cation composition of 53% La, 47 % Fe with a standard deviation of 2. It corresponds to the same mean composition that was measured for the LaFeO_3 /Si thin films deposited under the same PLD conditions [14]. Several line scans were performed to reveal possible chemical composition fluctuations in the LaFeO_3 layer. Line scans along the growth direction (Fig. 5b), or parallel to the substrate (Fig. 5c) always showed an iron deficiency in the layer composition. The fact that the iron under stoichiometry was more pronounced near the surface of the layer (Fig. 5b) may be attributed to a preferential thinning phenomenon. The cation composition of the layer is homogeneous from the substrate to the top of the layer, as well as along the layer, despite the observed composition variations, up to 10%. Indeed, these fluctuations occur between positions separated from 1 nm, so can unambiguously attributed to an acquisition phenomenon, and are not related to a real composition variation.

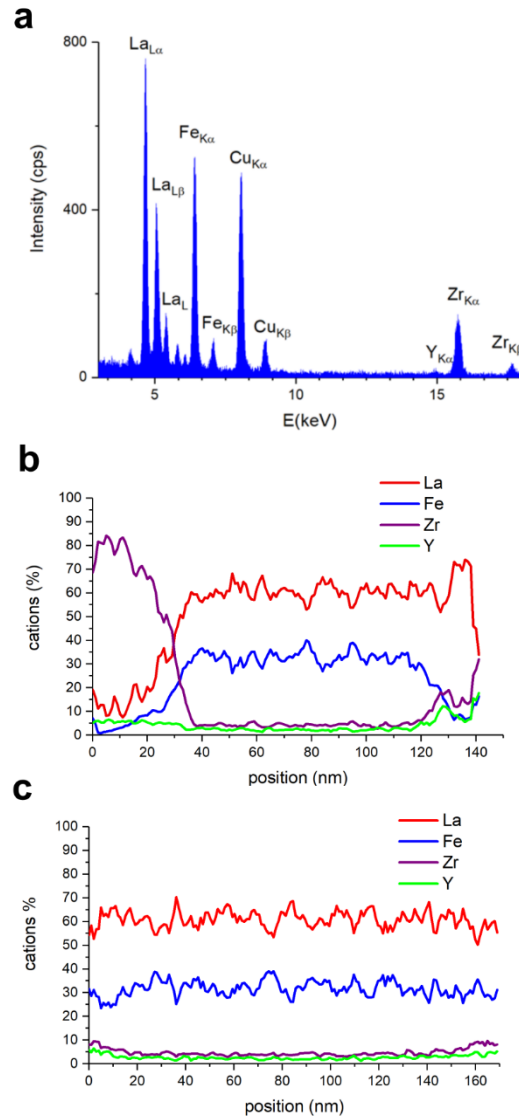


Figure 5. Energy dispersive spectroscopy. a) local EDS spectrum, showing the peaks characteristic of La and Fe, b) line scan from the substrate to the top of the LaFeO₃ layer, c) line scan in the LaFeO₃ layer perpendicular to the growth direction.

Raman spectroscopy (Fig. 6) was performed on the LaFeO₃-850/T-YSZ sample as well as on the bare T-YSZ substrate; this later spectrum was subtracted from the LaFeO₃-850/T-YSZ spectrum to remove the substrate contribution, using a renormalization factor [32]. Fig. 6a shows the raw spectra acquired at two different wavelengths in order to distinguish Raman peaks from the fluorescence ones. The data acquired with the 488nm wavelength (close to the LaFeO₃ absorption band range), led to the Raman spectrum presented in Fig. 6b (red line). This spectrum is in good agreement with the LaFeO₃/SiO₂/Si (100) thin film spectrum acquired with a laser wavelength of 488 nm [32] (blue line in Fig. 6b,) and the LaFeO₃ powder spectrum acquired with a laser wavelength of 514 nm [33] (yellow line in Fig. 6b).

The three series of peaks in the 100-200 cm^{-1} , 250-350 cm^{-1} , 400-450 cm^{-1} ranges are the characteristic LaFeO_3 first-order modes [34,35], and the peaks in range 1100-1400 cm^{-1} correspond to second order modes [33]. According to first-principles calculations [36] and Raman measurements under temperature-controlled hydration [37], the peak detected at 620-680 cm^{-1} is a signature of vacancies in the LaFeO_3 layer, in agreement with the EDS analyses.

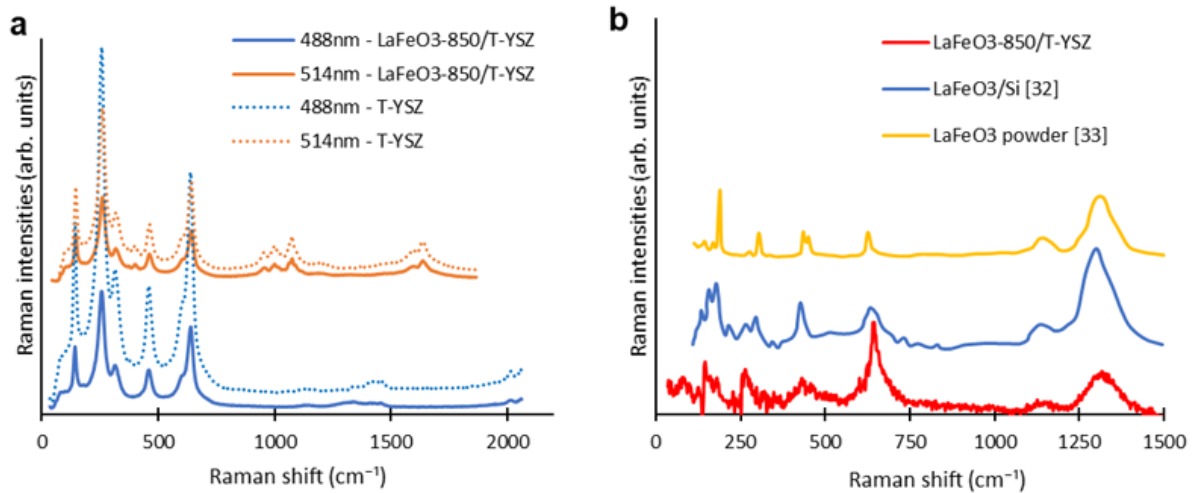


Figure 6. Raman spectroscopy a) Raw spectra of LaFeO_3 -850/T-YSZ (straight lines) and of the T-YSZ substrate (dot lines) using two different wavelengths (488 nm blue lines and 514 nm orange lines) b) Raman spectrum of the LaFeO_3 layer (red line) deduced from the raw data, compared to Raman spectra of LaFeO_3 thin film deposited on Si(100) [32] (blue line) and of LaFeO_3 powder (yellow line) [33].

3.4 Atomic-scale microstructure of the LaFeO_3 thin films

STEM-HAADF imaging of the LaFeO_3 layer was performed to investigate the microstructure of grains, in particular their growth direction as well as exposed facets, but also to gain information on the curvature accommodation.

Bunches of LaFeO_3 grains with the same zone axis were grown whatever the curvature of the substrate, as can be seen in Fig. 7 and Fig. 8. High resolution STEM HAADF allowed to image the La and Fe cations columns (insert in Fig. 7). The two FFT inserts in Fig. 7, carried out on two adjacent grains, in the region where the curvature of the substrate is at his maximum, show two variants oriented at 90° , with the same zone axis [1-10]. In one case, the growth direction is along the [110] axis, and in the other case, along [010]. Let us remind that these orientations correspond respectively to $[001]_c$ and $[100]_c$ of the pseudo perovskite cubic cell. This type of domains is quite common in LaFeO_3 and are known to be separated by {112} twins [38]. Such twins were not observed in LaFeO_3 thin films grow on Si [14] and can be related to an

adaptation of the curvature of the T-YSZ substrate. The terminations of the grains are rather flat, with $\{110\}$ or $\{010\}$ exposed facets. In regions with minor curvature of the substrate, (right part of Fig.7) one observes a tilt of a few degrees between two adjacent grains.

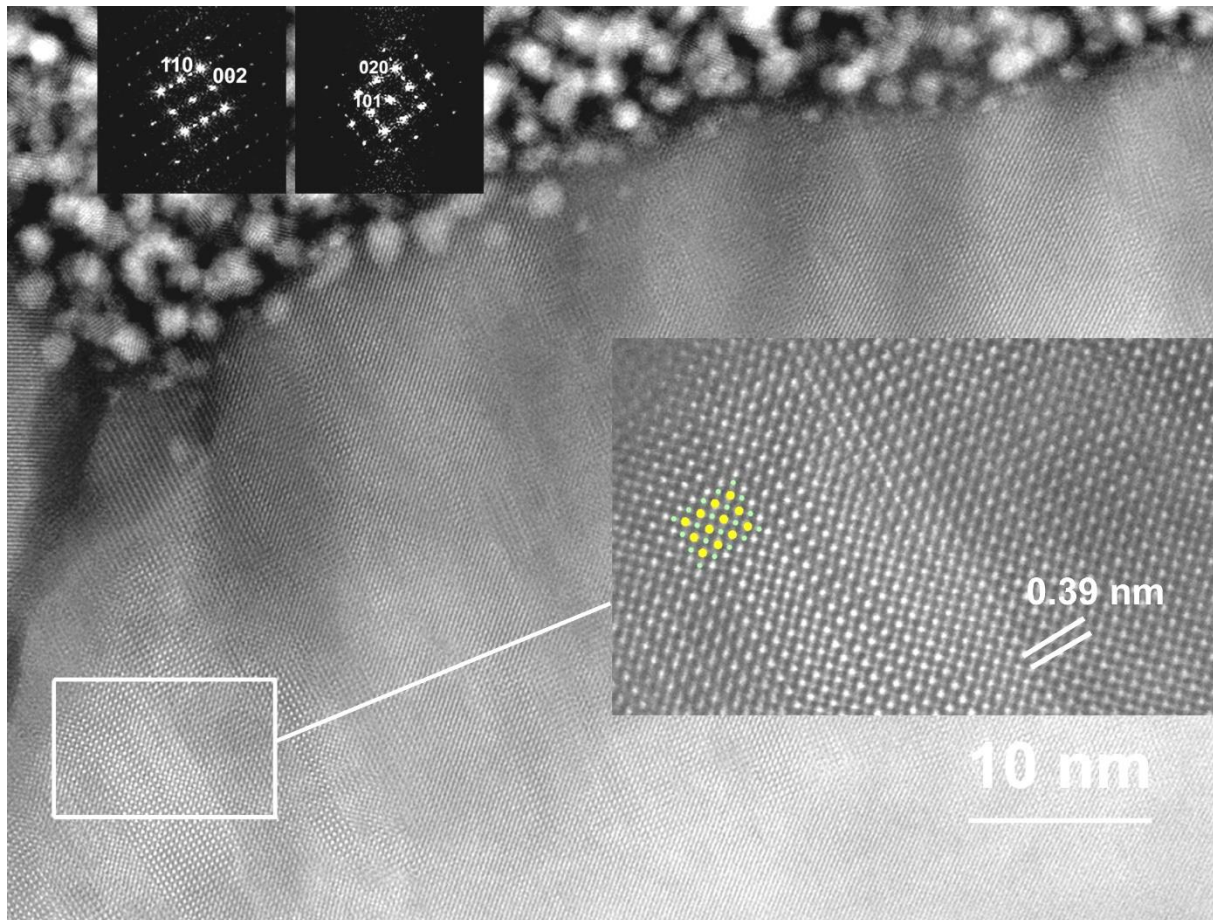


Figure 7. STEM-HAADF image of $\text{LaFeO}_3\text{-850/T-YSZ}$ in a highly curved region. The chemical contrast allows to image columns of La and Fe cations. The projected structure is superimposed in the insert (La in yellow and Fe in green).

Tip-like termination for LaFeO_3 grains were also observed (see Fig.8). In that case, the growth direction is $[110]$ and the exposed facets $\{010\}$ or $\{100\}$.

If one compares the exposed facets and shapes of the LaFeO_3 grains grown on T-YSZ with those grown on Si [14], it appears that tip-like or flat-ended terminations are the privileged shapes for LaFeO_3 grains grown by PLD, whatever the substrate. From the comparison, one can also conclude that the $[110]$ and $[010]$ are the two main growth directions. However, the link between shape of the grain termination and exposed facets is not the same. For tip-like grain terminations, the exposed facets are $\{010\}$ and $\{100\}$ with a $[110]$ growth direction for

LaFeO₃-850/T-YSZ, as for LaFeO₃-850/Si, the exposed facets are {110} and {-110} with a [010] growth direction [14]. In terms of pseudo cubic perovskites cell, this means that the LaFeO₃ grown on T-YSZ substrate grains exposed mainly flat {010}_c facets and tip-like {110}_c facets.

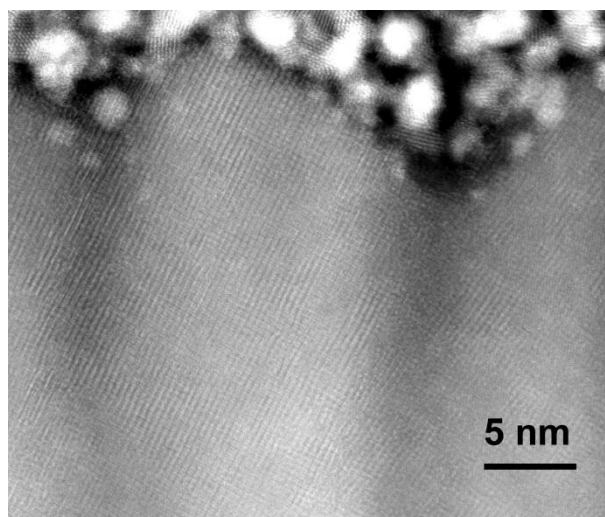


Figure 8. STEM-HAADF image of LaFeO₃-850/T-YSZ grains oriented with a [001] zone axis, showing tip like terminations of LaFeO₃ grains.

Conclusion

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Acknowledgments :

This work was realized with a Ph.D. scholarship of the French embassy in Poland. The TEM research has received funding from the European Union's Horizon 2020 research and innovation program under Grant agreement ESTEEM3. Authors would like to thank C. Pardanaud for fruitful discussions.