Epitaxial growth and cationic exchange properties of layered \( \text{KNb}_3\text{O}_8 \) thin films†

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The \( \text{KNb}_3\text{O}_8 \) potassium trinitoate phase is a layered compound that shows excellent photocatalytic activity, intercalation properties and electrochemical performances. In this study, we report the synthesis of this niobate in thin film form. Thin films of layered \( \text{KNb}_3\text{O}_8 \) phase were grown by pulsed laser deposition on (100)-oriented strontium titanate \( \text{SrTiO}_3 \) substrates using targets with different compositions and various deposition parameters. Samples were analyzed by X-ray diffraction, scanning and transmission electron microscopy, X-ray energy dispersive and Rutherford backscattering spectroscopies. This work shows that \( \text{KNb}_3\text{O}_8 \) films are obtained in a narrow composition range, close to \( \text{K}_{1.13}\text{Nb}_3\text{O}_8 \). That can be achieved with several combinations of the elaboration parameters (target composition, deposition temperature, target–substrate distance, laser fluence). Slight potassium amount variations in the film composition lead to the growth of other niobiates (i.e. \( \text{K}_2\text{Nb}_2\text{O}_5 \), \( \text{K}_6\text{Nb}_{10.88}\text{O}_{30} \), \( \text{K}_3\text{Nb}_2\text{O}_{12} \), \( \text{K}_2\text{Nb}_6\text{O}_{17} \)). The \( \text{KNb}_3\text{O}_8 \) films are either made of elongated crystals (500 nm long, 50–75 nm wide, and 40 nm thick) or of flat lamellae. In both cases, they are (010)-preferentially oriented with epitaxial relationships with the substrate, namely (010)\( \text{KNb}_3\text{O}_8/(100)\text{SrTiO}_3 \), (001)\( \text{KNb}_3\text{O}_8/(010)\text{SrTiO}_3 \) and [001]\( \text{KNb}_3\text{O}_8/[001]\text{SrTiO}_3 \). Protonation of the \( \text{KNb}_3\text{O}_8 \) films leads to a complete exchange of \( \text{K}^+ \) ions by \( \text{H}_3\text{O}^+ \) ions that are themselves exchanged by \( \text{Sn}^{2+} \) ions after immersion in a tin chloride solution confirming the exchange reaction capabilities also in thin films. Exchange of \( \text{K}^+ \) by \( \text{Sn}^{2+} \) leads to the band gap reduction of 0.33 eV.

1. Introduction

Layered compounds have received considerable attention for several years due to their numerous catalytic properties, such as intercalation and exfoliation, induced by their particular structure.1–4 Among these compounds, the \( \text{KNb}_3\text{O}_8 \) potassium trinitoate phase (see crystal data in Table 1;5 energy gap: 3.7 eV)6 shows luminescence,7,8 and excellent UV photocatalytic activity for degradation of dyes,9,10 for catalytic synthesis of organic contaminants,11,12 for decontamination of water,13,14 the formation of a p-n heterojunction with high performance under visible light for \( \text{H}_3\text{ONb}_3\text{O}_8 \),14,15 several routes have been used to synthesize \( \text{KNb}_3\text{O}_8 \) as single crystal by Czochralski and Bridgman-type methods,14,15 and as powder by solid state chemistry,16,17 molten salts synthesis,17,18 hydrothermal synthesis,17 solvothermal synthesis,19,20 and electrochemical

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2. Experimental section

2.1. Synthesis

Thin films were grown by PLD using a KrF excimer laser (Coherent COMPeXPro 102F, pulse duration 20 ns, λ = 248 nm) operating at 2 Hz with an energy of 210 mJ at two fluence values (1.85 and 1.95 J cm⁻², respectively). The target–substrate distance 𝑅𝑇𝑆 range was 50–70 mm. During the deposition (30 min), the oxygen pressure (0.3 mbar) was kept constant. Indeed, our previous work on niobates showed that this pressure is favorable to a good quality of crystallization.⁴⁵ In the same way, the substrate heater temperature (𝑇) was fixed at 700 °C.

The substrates were 5 × 5 mm² single crystal (100)SrTiO₃ ((100)STO), Joint Committee on Powder Diffraction Standards (JCPDS) card no. 01-073-0661; 𝑃𝑛3𝑚 (no. 221); 𝑎 = 3.905 Å) supplied by Crystal GmbH Company, and were ultrasonically cleaned in acetone during 5 min, then in isopropyl alcohol during 5 min prior to the deposition. Table 2 lists the deposition parameters of 6 of the samples (denoted A to F) synthesized in this study. In order to evaluate the band gap of films before and after cation exchange (see below), a KNb₂O₅ film was grown on a 2 polished faces 10 × 10 × 0.5 mm SiO₂ substrate supplied by Crystec company. The deposition procedure on this substrate was the same as the one used for film F on STO substrate.

As noted in the introduction, the target composition plays an important role in the film composition, and targets with different compositions were used in this work. These PLD targets were prepared by solid state reaction from Nb₂O₅ and K₂CO₃ precursors at 1000 °C in air during 12 h and this synthesis was followed by a sintering of the obtained mixture in air at 1000 °C during 6 h. The precursors were supplied by Alfa Aesar and Acros, respectively. The relative proportions of precursors were prepared with the purpose to obtain targets with various relative cations contents. The target compositions were K₀.₄₅NbO₂.₅ (i.e. K₁.₃₅NbO₂.₅) and K₀.₅NbO₂.₅ (i.e. K₀.₅NbO₂.₅). Therefore, the ratio between cations amounts (K/Nb ratio) in the targets is equal to 0.45 or 0.5. The real target compositions were measured by energy dispersive X-ray spectroscopy and were found to correspond to what was expected, i.e. K₀.₄₅NbO₂.₅ and K₀.₅NbO₂.₅. Prior to the deposition, the targets...
were polished on dry 320 and 1200 grit SiC papers and cleaned by pulsed dry nitrogen.

2.2. Characterization methods

Samples were observed by scanning electron microscopy (SEM) with two field emission gun Jeol JSM 6310F and Jeol JSM 7100 TTLS instruments working at 7 kV, and at 2 and 5 kV, respectively. Chemical composition of the samples was determined by energy dispersive X-ray spectroscopy (SEM-EDXS) by using a Jeol JSM 6400 instrument operating at 10 kV equipped with an Oxford Inca EDXS system. The samples were coated with carbon prior to this analysis. X-ray diffraction (XRD) characterization of obtained thin films was carried out using a θ–2θ instrument (Bruker AXS D8 Advanced) working with a monochromatized Cu Kα1 radiation and equipped with a 1D detector (192 channels). Data were collected across a 2θ range of 5–80°, using a step of 0.014° and acquisition time of 180 ms per step. Thin films epitaxy study was carried out using a four circle texture diffractometer (Bruker AXS D8 Discover) operated with Cu Kα radiation in θ–2θ, ω-scan and φ-scan modes, equipped with a 1D detector (192 channels). Transmission electron microscopy (TEM) experiments were performed by using a LaB₆ Jeol 2100 instrument equipped with an Oxford Aztec 80 mm² SDD device for EDXS analysis (TEM-EDXS). Samples for TEM 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). Transmission electron brightfield, darkfield micrographs, and electron diffraction patterns were recorded using a GATAN Orius200D CCD (charge coupled device) camera. Rutherford backscattering spectroscopy (RBS) which is well suited for the determination of the composition and thickness of thin films has been used to study the potassium triinobate layers obtained by PLD. For such analyses, a R-plane sapphire substrate (1-102)Al₂O₃, (JCPDS card no. 00-010-0173; R3c (no. 167); a = 4.758 Å, c = 12.991 Å) was used instead of SrTiO₃, to avoid the overlapping of the K and Sr and Ti contributions in the RBS spectra. The elaboration parameters of films on sapphire were: target composition K₀.₄⁵NbO₂.₅, DTS = 60 mm, duration = 10 min (in order to obtain a film thickness about 100 nm, which is mandatory for RBS experiment), fluence = 1.85 J cm⁻² and T = 700 °C. The RBS experiments were carried out with a 2 MeV He⁺ ion beam. Absorbance spectra were registered with a UV-Visible Perkin-Elmer and an infra-red UATR Frontier Perkin-Elmer spectrometers, using a SiO₂ substrate as reference.

2.3. Protonation and exchange properties

Ion-exchange of KNb₃O₈ thin films was attempted by using two different methods. A KNb₃O₈ film was immersed in a 0.08 M HCl/SnCl₂ solution for 9 days at room temperature (RT) in order to exchange K⁺ for Sn²⁺ (HCl acid was used to avoid the precipitation of the tin chloride). The film was daily rinsed with distilled water, dried in air, and analyzed by XRD. No change was observed except degradation of the film the last day of the immersion. A second KNb₃O₈ thin film (film F) was immersed in a 6 N HNO₃ solution for 24 h at RT to exchange KNb₃O₈ for H⁺, then rinsed with distilled water and dried in air, the result of which is referred as film F2. This film was analyzed by XRD and TEM-EDXS. In a second time, the film was immersed in a 0.08 M HCl/SnCl₂ solution for 64 h at RT in order to exchange H₂O⁺ for Sn²⁺. During this experiment, the film was daily rinsed and dried and analyzed by XRD, and subsequently re-immersed in a fresh HCl/SnCl₂ solution (film F3). After 64 h, the ion exchange was checked by TEM-EDXS. The same procedure was used with the film grown on silica.

3. Results and discussion

3.1. Growth, phase analysis and morphology

In addition to the KNb₃O₈ phase, there exist several potassium niobates in the Nb₂O₅–KNbO₃ phase diagram:⁴⁶ K₂Nb₃O₉,⁴⁷ K₂NbO₇-⁴⁹ tetragonal tungsten bronze (TTB) K₆Nb₁⁰.₈₈O₃₀ phase,⁴⁶ and K₃Nb₇O₁₉ (see crystal data in Table 1). In this study, more than 20 samples made of either pure KNb₃O₈ phase or KNb₅O₉ phase with these other potassium niobates were synthesized with different combinations of growth parameters: target–substrate distance DTS, substrate temperature T, target composition, laser fluence. In the following, the characterization results of 6 of these samples (denoted films A to F in Table 1) are summarized. The Fig. 1 shows the Nb₂O₅–KNbO₃ line (in black) on which the compounds of the phase diagram were reported according to the value of K on Nb ratio (K/Nb ratio) for each of them. From EDXS results, positions of the films were added in red, while positions of the targets appear in blue. The decrease of the K amount relatively to that of Nb in the film compared to that of the target, is due to the volatility of K₂O at the deposition temperature.⁴⁵ From the XRD, SEM and SEM-

| Sample | Temperature (°C) | Target–substrate distance DTS (mm) | Fluence (J cm⁻²) | Target composition | Film composition | K/Nb ratio in the film | Phases |
|--------|-----------------|-----------------------------------|-----------------|-------------------|-----------------|-----------------------|--------|
| A      | 700             | 50                                | 1.85            | K₀.₅NbO₂.₅, (K₁.₅NbO₂.₃) | K₁₈₋₂₀.₁₂NbO₄   | 0.39                  | KNb₃O₈ + K₂NbO₇ + K₉Nb₉.₈₈O₃₀ |
| B      | 700             | 55                                | 1.85            | K₀.₅NbO₂.₅, (K₁.₅NbO₂.₃) | K₁₁₋₂₀.₁₁NbO₄   | 0.37                  | KNb₃O₈ + K₂NbO₇ + K₉Nb₉.₈₈O₃₀ |
| C      | 700             | 65                                | 1.85            | K₀.₅NbO₂.₅, (K₁.₅NbO₂.₃) | K₁₂₋₁₁.₉NbO₄   | 0.33                  | KNb₃O₈ + K₂NbO₇ + K₉Nb₉.₈₈O₃₀ |
| D      | 700             | 70                                | 1.85            | K₀.₄NbO₂.₅, (K₁.₅NbO₂.₃) | K₀.₉₋₁₀.₁NbO₄   | 0.30                  | KNb₃O₈ + K₂NbO₇ + K₉Nb₉.₈₈O₃₀ |
| E      | 700             | 70                                | 1.95            | K₀.₅NbO₂.₅, (K₁.₅NbO₂.₃) | K₀.₉₋₁₀.₁NbO₄   | 0.30                  | KNb₃O₈ + K₂NbO₇ + K₉Nb₉.₈₈O₃₀ |
| F      | 700             | 65                                | 1.95            | K₀.₅NbO₂.₅, (K₁.₅NbO₂.₃) | K₁₋₁₂.₉NbO₄    | 0.33                  | KNb₃O₈   |
EDXRS characterization results, it comes that the phase is obtained when the film composition corresponds to a K/Nb ratio $\sim 0.30–0.37$, therefore around the stoichiometric composition (K/Nb ratio = 0.33). The RBS analysis (Fig. S11 ESI†) performed on a pure KNbO$_3$ film gives the K$_{1.11}$Nb$_{0.89}$O$_8$ composition (K/Nb ratio = 0.376); this value is close to the stoichiometric formula and close to the result found by EDXRS (K$_{1.11-\pm 0.1}$Nb$_{0.89-\pm 0.1}$O$_8$ and K$_{1.00\pm 0.1}$Nb$_{0.5}$O$_2$ for films B and F, respectively). In all cases, the KNbO$_3$ phase grows on (100)STO with the [010] preferential orientation, i.e. with the Nb$_3$O$_8^{-}$ layers parallel to the substrate surface, and no other orientation is observed. The value of the parameter $b$ was measured to be 21.2 Å for all the films, i.e. close to the refined parameter ($b = 21.2118$ Å) determined by Madaro et al.\textsuperscript{35} In addition to the KNbO$_3$ phase, the growth of the K$_4$Nb$_8$O$_{17}$ and K$_8$Nb$_{10.88}$O$_{30}$ phases is observed (film A, Fig. 2a, Table 2) when the target of composition K$_{0.45}$Nb$_{0.55}$O$_{2.5}$ is used together with a target–substrate distance $D_{TS} = 50$ mm.

Thus, the amount of potassium in this film is too high for the targeted compound. It is surprising to observe the growth of the K$_4$Nb$_8$O$_{17}$ phase since the composition of the film if far from that of this compound. Actually, we have observed that this phase has the ability to grow in a very large composition range.\textsuperscript{29} To decrease the amount of potassium relatively to that of Nb, a film was synthesized with a higher target–substrate distance ($D_{TS} = 55$ mm, film B, Fig. 2b). Film B is mainly constituted of the KNbO$_3$ phase. Displaying the intensity of the diagram in logarithmic scale allows to observe a peak located at $2\theta = 22.31^\circ$ ($d = 3.98$ Å), the intensity of which is 160 counts per s while that of the (020)KNbO$_3$ peak is 88 500 counts per s. This peak corresponds to the (001)K$_2$Nb$_{10.88}$O$_{30}$ TTB phase, which is therefore still present. From this configuration, additional increase of $D_{TS}$ (Fig. 2c, film C) leads to a depletion of potassium in the film and to the growth of the K$_4$Nb$_8$O$_{17}$ niobate.\textsuperscript{31,53} Using a target with a lower K amount (films D and E, target K$_{0.45}$Nb$_{0.55}$O$_{2.5}$, $D_{TS} = 70$ mm) also leads to the growth of the KNbO$_3$ phase together with a small amount of K$_5$Nb$_{6}$O$_{21}$ (Fig. 2d and S11†). For these two films, the presence of K$_5$Nb$_{6}$O$_{21}$ is not observed in the XRD diagrams but is evidenced by SEM micrographs (see below). Finally, pure KNbO$_3$ films were obtained from the same target of composition K$_{0.45}$Nb$_{0.55}$O$_{2.5}$ with a lower target–substrate distance ($D_{TS} = 55$ mm, film F, Fig. 2e). SEM micrographs display that the microstructure of KNbO$_3$ on STO, for all samples synthesized with a fluence fixed at 1.85 J cm$^{-2}$ (films A–D), is made of elongated and parallelepiped-shaped crystals of dimensions 500 nm in length, and 50–75 nm in width (Fig. 3a–c and S12 ESI†). Two variants of elongated crystals are observed, corresponding to two in-plane orientations (marked by blue arrows in Fig. 3b), one growing parallel to the [010]STO direction, and the other one at 90° in regards to the first variant.

The samples made at fluence of 1.95 J cm$^{-2}$ (films E and F) have a different morphology. Indeed, they are constituted of macroscopic flat lamellas that are irregular in shape but higher in dimensions (0.5–1 µm) (Fig. 3d). It has been reported that when the fluence is higher, the kinetic energies of ablated species are increased. As a consequence, the fluence is known to affect the growth mode of the film, that follows either the Volmer-Weber mode, with islands formation, (3 dimensions (3D) growth), or Frank–van der Merwe mode (layer-to-layer formation, 2D) or Stranski–Krastanov mode (2D + 3D).\textsuperscript{24,55} In the present case, the microstructures displayed in Fig. 3a–c would correspond to the first growth mode, and the morphology of the parallelepiped crystals reflects the anisotropy of the crystal structure. Madaro et al.\textsuperscript{35} have synthesized KNbO$_3$ plate-like crystals by molten salt synthesis and shown that morphology of crystals depends both of temperature and salt/oxide weight ratio. They have evidenced that the plates have the [010]-preferential orientation and that the length of the plates grows along the [001] direction. They suggested that this direction which corresponds to the lower connectivity between the corner-sharing NbO$_6$-octahedra, is perpendicular to the facets with lower surface energy. Indeed, the particle shape is thermodynamically controlled by the Wulff construction which is the surface that minimizes the total surface free energy of a crystal, as a function of crystallographic orientation.\textsuperscript{24} Therefore, crystals with anisotropic crystalline structure have generally an anisotropic shape.\textsuperscript{57} In the case of flat lamellas (films E
and F), the growth mode would follow the Frank–van der Merwe mode and the anisotropy of the crystal dimensions is also present, but the films being very flat, the SEM contrast is very low and limits the observation. The thicknesses of the films B and E are about 205–215 nm and 120–135 nm, respectively (Fig. SI3 ESI†).

3.2. Transmission electron microscopy characterization

As shown above, depending on the fluence as a unique parameter, two types of films were observed, differing strongly in their morphology. Also, SEM photographs show some outgrowths perpendicular to the film surface. TEM was used to characterize these features.

3.2.1. Parallelepiped-shaped films. The Fig. 4a displays a brightfield (BF) micrograph of some KNb$_3$O$_8$ crystals collected from a KNb$_3$O$_8$ thin film (film D). The corresponding electron diffraction pattern (EDP) (Fig. 4b) shows that the elongation direction of the plate is [001] that confirms the results of Madaro et al. and of Kong et al. on KNb$_3$O$_8$ particles. Therefore, the shortest lattice parameter $c$ is parallel to the longest crystals edge, as also observed for the anisotropic K$_2$Nb$_{10.88}$O$_{30}$ TTB phase. The measured lattice parameters by electron diffraction, reported to that of the substrate used as internal standard, are $a = 8.93$ Å and $c = 3.79$ Å, also close to the values refined by Madaro et al. in the case of powders. In this EDP, one can observe thin diffusive lines parallel to the KNb$_3$O$_8$ [100]$^*$ direction highlighted by white dashed lines in the Fig. 4b and characterized by $d \sim 4$ Å (see inset in Fig. 4b). In order to more clearly evidence these lines of diffusive scattering, a KNb$_3$O$_8$ crystal was slightly tilted from the [010] zone axis. Darkfield (DF) micrographs (Fig. 4c and d) were then recorded.
by selecting the 200 reflection of the KNb$_3$O$_9$ phase (inset in Fig. 4c) and a segment of one of the diffusive line (inset in Fig. 4d). These micrographs show that the crystal is actually constituted of stratified layers of well-crystallized KNb$_3$O$_9$ slabs that alternate with slabs that are parallel to the (100)KNb$_3$O$_9$ planes. These slabs are another phase that is disordered in the plane parallel to (100)KNb$_3$O$_9$. Lundberg and Sundberg have also reported very faint streaked pattern of KNb$_3$O$_9$ (denoted L-KNb$_3$O$_9$ in their work) and have observed that this phase transforms in the solid state to TTB-related phases through an amorphous or poorly crystallized intermediate stage. This phase is possibly the KNb$_3$O$_9$ phase, which is a pseudo-superstructure of the TTB phase.\(^{23}\) Indeed, $d_{001}$ for K$_2$Nb$_8$O$_{21}$ phase is equal to 3.95 Å, and this phase is next to the KNb$_3$O$_9$ phase in the phase diagram. The TEM-EDXS analysis performed on several KNb$_3$O$_9$ crystals gives the K$_{1.14}$Nb$_{0.12}$O$_8$ composition (K/Nb ratio $\approx 0.38$) in agreement with the previous composition analysis.

### 3.2.2. Flat lamellas films

BF micrograph in the Fig. 4e confirms that the crystals are made of stacking of thin lamellas that are electron transparent, therefore few dozens of nanometers thick. The corresponding EDP (Fig. 4f) shows the [010] zone axis pattern in which no diffuse line is observed, in contrast to film D. Since films D and film E, with same composition, were synthesized with the same deposition parameters except for the fluence, it turns out that this parameter plays also a major role in the crystallinity of the film in addition to its morphology. According to the TEM results of Sundberg and Lundberg,\(^{29}\) Madaro et al.\(^{35}\) and Liu et al.,\(^{36}\) very thin KNb$_3$O$_9$ plates are well-crystallized, as for the films E and F made of thin lamellas. Therefore, it could be emphasized that the parallelepipedic shape of KNb$_3$O$_9$ crystals in films A to D is related to the intergrowth of poorly crystallized slabs/KNb$_3$O$_9$ slabs. Liu et al. have evidenced that photocatalytic performances of KNb$_3$O$_9$ compound depend on the crystals shape, and consequently the exposed faces. Indeed, they have shown that very thin flat sheets synthesized by hydrothermal method exhibit higher photocatalytic properties than rod-like crystals synthesized by molten salt method.\(^{37}\) Therefore, effect of the fluence on the morphology of the thin film crystals is of first importance for their properties.

### 3.2.3. Identification of outgrowths

On Fig. 3b, one can observe the presence of larger and non-oriented outgrowths on the KNb$_3$O$_9$ film, marked by a white arrow. Combination of electron diffraction and darkfield micrographs (TEM experiments) have evidenced that these crystals are nanostructures made of the K$_2$Nb$_{10.88}$O$_{19}$ TTB rods (in agreement with our previous results)\(^{38}\) on which rectangular K$_2$Nb$_{17}$O$_{17}$ plates have grown (not shown).\(^{32}\) This will be the subject of another article on the growth of the KNb$_3$O$_9$ phase. The TTB rods are (001) preferentially oriented, and correspond to the small (001) XRD peak in Fig. 2b. In Fig. 3c and in inset, one can observe the growth of thin vertical ribbons with their elongation direction parallel to the out-of-plane direction. Similarly, vertical nanorods are observed in Fig. 3d and inset. The dimensions of the nanoribbons are 10–40 nm in width and 400–500 nm in length, while the nanorods are wider (50 nm) and shorter (300 nm).

Electron diffraction experiments (Fig. 5b), performed on 10 different nanoribbons and 10 different nanorods, have evidenced that these nanoribbons and nanorods are actually made of the K$_2$Nb$_{17}$O$_{17}$ phase, with the [001] direction parallel to elongation direction (Fig. 5a), that corresponds to the peak located at $2\theta = 22.42^\circ$ ($d = 3.96$ Å) in the XRD pattern (Fig. 2c). Most of these nanoobjects present structural disorder along (001) planes, as evidenced by diffuson lines in the electron diffraction pattern (Fig. 5b). These results are in agreement with the work of Xu et al. who have synthesized nanoribbons and nanorods of this phase by a molten salt route.\(^{36,37}\) Recently, Paria Sena et al. have solved the crystalline structure of the KNb$_3$O$_9$ phase in the K--Nb--Ta--O system, and demonstrated that this structure is a pseudo-superstructure of the TTB phase, with the following lattice parameters $a \approx 2\sqrt{2}a_{TTB} \approx 37.4$ Å, $b \approx b_{TTB}$, and $c \approx c_{TTB}$.\(^{31}\) Therefore, both TTB phase and its superstructure have the same growth behavior, i.e. very anisotropic crystal growth with their [001] out-of-plane growth direction corresponding to their elongation direction. Accurate study of the growth of TTB nanorods and of K$_2$Nb$_3$O$_{21}$ nanoribbons will be the subject of another article.\(^{32}\)

![Fig. 5](image-url) (a) BF micrograph of a K$_2$Nb$_3$O$_{21}$ vertical ribbon. (b) Corresponding EDP along the [100] zone axis. Dashed lines show diffusive lines present in the pattern.
or amorphous substrates will lead to the [010] preferential epitaxy, in which relationships belongs to the frame of the domain matching units of the substrate. The values of \( \theta \) on the substrate, orientations of KNb\(_3\)O\(_8\) crystals on (100)STO (view along the normal to B). (b) Scheme of (100)STO substrate and of the two corresponding orientations of KNb\(_3\)O\(_8\) crystals on (100)STO (view along the normal to the substrate, i.e. along the [010] direction of STO, and along the [010] direction of the KNb\(_3\)O\(_8\) phase). The variant 1 is clamped on the substrate in reason of the low mismatch between its c edge relatively to that of the c edge of STO (red segments). The same phenomena is observed for variant 2 (c edge close to b edge of STO, blue segments).

Epitaxial growth is due on one hand to the low mismatch between the lattice parameter of the substrate and the c parameter of KNb\(_3\)O\(_8\) \((d_{\text{STO}} - c_{\text{KNb,O}_8})/a_{\text{STO}} \times 100 = 2.7\%\), and on the other hand, to the low mismatch between 9 lattice units of the substrate and 4 lattice units of the film along the second parameter \((9a_{\text{STO}} - 4a_{\text{KNb,O}_8})/(9a_{\text{STO}}) = -1.33\%\). This last relationships belongs to the frame of the domain matching epitaxy, in which \( m \) lattice units of the film match with \( p \) lattice units of the substrate. The values of \( m \) and \( p \) are defined as the minimum integers which satisfy the relation: \( m d_{\text{KNb,O}_8} = p d_{\text{STO}}, d_{\text{KNb,O}_8} \) and \( d_{\text{STO}} \) being the respective atomic distances in the film and substrate parallel directions.52,63

The rocking-curve (ω-scan) around the 020 reflection of KNb\(_3\)O\(_8\) reveals a medium value of the mosaicity \( (\Delta \omega = 1.1^\circ \) for film B, and \( 1.85^\circ \) for film E, whereas for STO \( \Delta \omega = 0.034^\circ \); Fig.S15 ESI†) showing some misorientation of this phase on the substrate.

It is probable that the growth of KNb\(_3\)O\(_8\) on polycrystalline or amorphous substrates will lead to the [010] preferential orientation as well, as for other lamellar phases with large interlamellar distance,64 but with no-ordering in the plane. Therefore, the ability of KNb\(_3\)O\(_8\) to grow with an in-plane orientation on a single-crystalline substrate is interesting to increase properties compared to those of textured films.

### 3.4. Exchange properties

Hosogi et al. have shown that the exchanged layered Sn\(^{2+}\)/K\(_2\)Nb\(_3\)O\(_8\) niobate had visible-range light absorption bands leading to photocatalytic properties under visible light, with a reduction of the energy gap from 3.5 to 2.8 eV.65 From these results, we studied the ability to exchange K\(^+\) by Sn\(^{2+}\) in KNb\(_3\)O\(_8\) films. Fig. 7 displays XRD patterns of the film F before protonation (Fig. 7a), after protonation (Fig. 7b and c) and after exchange experiments (Fig. 7d). After a day in nitric acid, the XRD peaks of the film F2 are noticeably shifted to lower angle values and splitted in 3 contributions, labelled by H, H‘ and H” in Fig. 7b. After a few hours in a desiccator, the film was re-examined by XRD, and in the resulting XRD pattern (Fig. 7c), both H’ and H” peaks have vanished or almost vanished while the intensity of the peaks H was considerably increased. The shift of the 020 peak corresponds to an increase of the interticular distance \( d_{020} \) from 10.59 to 11.23 Å, therefore to an increase of the interlamellar spacing from 21.18 to 22.46 Å. This increase is due to the larger size of the H\(_3\)O\(^+\) ion (280 pm, hydrated value) compared to that of the K\(^+\) ion (152 pm). This result is in full agreement with what was observed for a KNb\(_3\)O\(_8\) powder after being exchanged in acid nitric to form the H\(_3\)ONb\(_3\)O\(_8\) phase (see Table 1) with an increase of the lattice parameter \( b \) to the value 22.47 Å.12,32,63

The presence of H’ and H” peaks is most likely due to the intercalation of some species that have induced swelling of the lattice, characterized by an increase of the lattice parameter \( b \) to 24.68 Å \((d_{020} = 12.34 \text{ Å})\) and 25.44 Å \((d_{020} = 12.72 \text{ Å})\), respectively. The vanishing of these H’ and H” peaks after the stay of the sample in anhydrous atmosphere for a few hours suggests that these intercalated species are probably water and/or

**Fig. 6** (a) ω-Scans of the (240) planes of the KNb\(_3\)O\(_8\) phase (green line) and of the (110) planes of the (100)STO substrate (grey line) (film B). (b) Scheme of (100)STO substrate and of the two corresponding orientations of KNb\(_3\)O\(_8\) crystals on (100)STO (view along the normal to the substrate, i.e. along the [010] direction of STO, and along the [010] direction of the KNb\(_3\)O\(_8\) phase). The variant 1 is clamped on the substrate in reason of the low mismatch between its c edge relatively to that of the c edge of STO (red segments). The same phenomena is observed for variant 2 (c edge close to b edge of STO, blue segments).

**Fig. 7** XRD diagrams in θ/2θ mode: (a) KNb\(_3\)O\(_8\) film (film F); (b) same film (F2) after 24 h in a HNO\(_3\) solution (6 N); (c) same film (F3) after 8 h in air in a desiccator; (d) same film after 64 h in a SnCl\(_2\)/HCl solution (substrate: *).
hydrated hydronium ions, as proposed by Takahashi et al. that have observed the same phenomena after the protonation of KTiNbO₅ niobate.⁶⁴ We performed infra-red spectrometry on a H₂ONb₂O₈ film just after protonation, and after few hours in a desiccator (Fig. SI6 ESI†). Some absorptions bands observed in the spectrum of the just-protonated film are not present for the dehydrated film, as it was reported for other crystalline hydrates, and attributed to water and/or hydrated hydronium ions.⁶⁷,⁶⁸ After dehydration, more matter intercalated with H₂O⁻ ions is afterwards diffracting, involving the increase of the peak H intensity in XRD diagram. The film F2 was analysed by TEM-EDXS and found to be fully free of potassium, demonstrating the total exchange of the potassium ions by the hydronium ions (Fig. SI7 ESI†). From TEM, the lattice parameters were measured as being a = 9.1 Å and c = 3.84 Å (Fig. SI8 ESI†). Fig. 7d shows the XRD pattern of the H₂ONb₂O₈ film subsequently immersed 64 h in a tin chloride solution (film F3). The evolution of the XRD patterns of this film was checked daily and was no longer modified after 3 days in the solution. It is observed that the 020 peak shifts now to a higher angle value, corresponding to a decrease of the intertetrical distance from 11.23 Å (b = 22.46 Å) to 10.45 Å (b = 20.9 Å). This result corresponds to the decrease of the radius of the intercalated ion (83 pm for Sn⁺) relatively to that of H₂O⁻. The Fig. 8a shows the EDP of a part of the film after the two exchange reactions, corresponding to the diffraction of several crystals. By using a smaller selected area aperture, contribution of both variants are separated in Fig. 8b and c. These patterns are close to that displayed in Fig. 4f, with the lattice parameters a = 9.23 Å and c = 3.93 Å that are slightly higher than the values of the parent phase H₂ONb₂O₈, and show that the crystallinity of the phase was preserved. DF micrographs taken by selecting a reflection for each variant (Fig. 8d and e) show that the microstructure built from of rectangular lamellas growing at 90° from each other is also preserved. The Fig. S17 ESI† shows the TEM-EDXS spectra of film F3 compared to that of the films KNb₂O₈ and H₂ONb₂O₈, demonstrating the complete exchange of K⁺ by Sn²⁺. The composition measured by TEM-EDXS is about Sn₀.₆Nb₂O₈, therefore close to what is expected for a complete exchange with respect of electroneutrality. These two exchange reactions were carried out at room temperature, without stirring and in a relative short time, relatively to other exchange reactions performed on powder that take 2–3 days for protonation⁶⁶,¹²,¹⁹ and several days for exchange.¹²,²¹

Fig. SI9 ESI† shows that the thin film grown on silica with the same deposition parameters than the film F grown on STO is a single-phase [010]KNb₂O₈ film. As emphasized above, the film is (010) preferentially oriented even if the substrate is amorphous. This film was successfully protonated before exchange of the potassium ions for the tin ions as shown in Fig. S19 ESI†. In order to determine if crystal damage results from the exchange, we have performed high resolution transmission electron microscopy (HRTEM) on the KNb₂O₈ film, and on the SnNb₂O₈ film (Fig. SI10 ESI†). The micrographs and their fast Fourier transforms show that the SnNb₂O₈ film does not present crystal damage. Fig. 9 shows the absorbance spectra of the KNb₂O₈ thin film grown on silica, before and after protonation, and after exchange. The spectra of the H₂ONb₂O₈ and Sn₀.₆Nb₂O₈ films are red-shifted relatively to that of the KNb₂O₈ film towards the visible range. The corresponding energy gap were estimated to be 3.9 eV for KNb₂O₈ film (for 3.7 eV for powder), 3.78 eV for H₂ONb₂O₈ film, and 3.57 eV for Sn₀.₆Nb₂O₈ film. The effect of Sn exchange on the oxide band gap value was previously studied for the other layered potassium niobate in this system, i.e. K₆Nb₆O₁₇ compound, by Hosogi et al.⁶⁶ These authors reported that the Sn²⁺/K⁺Nb₁₇ gap was 0.7 eV narrower than that of K₆Nb₆O₁₇, while in the present work, Sn₀.₆Nb₂O₈ film gap was narrower of only 0.33 eV. Nevertheless, these first results are promising for synthesis of
exchange-Nb$_3$O$_8$ films with visible-range activity. According to the large amount of species that were intercalated in KNb$_3$O$_8$ powder in the past, the present results are also promising for formation of new intercalated KNb$_3$O$_8$ thin films for numerous applications as catalysis, electrochemistry, depollution of waste water, etc. In addition, lamellar-shaped films are expected to show better photocatalytic properties than the rod-shaped films. Indeed, the effect of the shape of powder KNb$_3$O$_8$ and HNb$_3$O$_8$ crystals on photocatalytic properties was recently studied by Li et al. and Liu et al.$^{56}$ Both groups found that belt shaped crystals present higher photocatalytic properties than the rod-like crystals.

4. Conclusions

Thin films of epitaxially grown KNb$_3$O$_8$ phase were synthesized by PLD, with the ability to change the morphology of the crystals constituting the film, from paralleliped-shaped rods to thin lamellas, by changing the laser fluence. The rods are actually built from alternated slabs of KNb$_3$O$_8$ phase and of a poorly crystallized K$_2$Nb$_3$O$_8$ phase. On the contrary, the lamellas are single phased and well-crystallized and present larger dimensions. We believe that this lamellar morphology of the film would be benefit on the properties as it was observed in the past for KNb$_3$O$_8$ crystals synthesized by molten salt method. The ability to exchange K$^+$ by H$_2$O$^+$ and then Sn$^{2+}$ was observed for KNb$_3$O$_8$ films, leading to potential properties based on intercalation of various species in the Nb$_3$O$_8$$^{2-}$ matrix as it was reported for powder. Perspectives of this work is to study these intercalation properties on cheaper polycrystalline and amorphous substrates, and also by low temperature deposition methods as chemical solution deposition.

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