Preparation of KNbO$_3$ thin films onto alumina substrates
by polymeric precursor method

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Abstract

This work presents the development of KNbO$_3$ powders and thin films prepared by the low-cost solution chemical method based on Pechini process. The influence of many synthesis parameters, such as coating solution viscosity, deposition method (dip- or spin-coating), [K/Nb] ratio, heat treatment and effect of multilayers deposition, on the phase formation and microstructure of thin films prepared onto alumina substrates were analyzed. It was verified that using a stoichiometric coating solution, K deficient films are formed. The K amount in the coating solution was increased in order to avoid this deficiency. Single-phased KNbO$_3$ samples were obtained at 550°C using solutions with [K/Nb] 1.25 and 1.50. These films are continuous, homogeneous and crack-free, and present a thickness about 100 nm per layer. The deposition of multilayers increases the film thickness, as well as it improves its homogeneity and density. Both deposition methods tested, spin- and dip-coating, lead to good results, after deposition parameters optimization. The best results are achieved using coating solution viscosity around $22 \times 10^{-2}$ P, dipping and withdrawing speed of 0.16 mm s$^{-1}$ for dip-coating and rotation rate around 3000 rpm during 20–40 s for spin-coating.

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1. Introduction

Ferroelectric materials are in a stage of rapid development due to their potential in large areas of microelectronics, micromechanics and optoelectronics. Among the large variety of ferroelectric perovskite-type oxides, potassium niobate (K NbO$_3$—hereafter—called KN) is already well known as a very promising material for ferroelectric [1,2], electro-optic [3] and non-linear optic [4] applications. For all these applications, high quality materials are needed and in most cases in thin film form to fit integration criteria. In particular, thin films are required for applications in microwave range, which appears as a large field of application of ferroelectric compounds. That is one important reason of the increasing number of publications related to KN thin films [5–11].

In spite of today’s existence of a rich literature dealing with thin films of KNbO$_3$, the most part of it concerns physical methods of preparation (Pulsed Laser Deposition [8,9], Sputtering [10,11], etc). These techniques are well developed and lead to satisfactory results. Nevertheless, they are expensive and require special equipment, as vacuum chamber and proper targets [12,13]. Chemical solution processes are alternative routes, such as sol–gel [14], amorphous complex [15] and polymeric precursor method based on Pechini process [16]. These methods present usually lower cost and easier manipulation strat-
gies. Moreover, they can give access to deposition on complex shape and wide area substrates and are low-temperature processes.

The concepts are almost the same for all the chemical solution methods: they are based on synthesis of a solution of some soluble metalorganic network, followed by elimination of the organic part (usually by calcination), in order to achieve the desired oxide. The main difficulty is the choice of the precursors, which in some cases requires manipulation under dry atmospheres, especially in the example of the use of metal alkoxides in sol–gel route. In contrast, the polymeric precursor method is carried out directly in aqueous media and uses no expensive metallic precursors, based essentially on citrate complexes (often obtained by the reaction between citric acid and metallic nitrates or carbonates). Moreover, it is already proven that it is possible to grow epitaxial thin films of high quality by this method [17,18].

In this context, the present paper is dedicated to the preparation, by the polymeric precursor method, and characterization of KN powders and thin films. Sintered alumina substrates have been chosen because these not expensive substrates are available in large area and are routinely used in microelectronics and especially in micro-waves field. One of the main parameters to control in order to achieve high quality samples is the [K/Nb] ratio. In fact, K losses occur by evaporation [19] in the range of temperature usually required for KN crystallization. On the other hand, an excess of K can lead to thin films that are moisture sensitive. Indeed, some authors have reported difficulty to avoid potassium rich or deficient deleterious phases [10,11,20–22]. Therefore, synthesis of well-crystallized KN thin films, avoiding the formation of any other secondary phase is the focus of this study. Other parameters, such as coating solution viscosity, thermal treatment and method of deposition are also discussed.

2. Experimental details

The synthesis of KN powders and thin films was based on the polymeric precursor method. This method consists of the preparation of a polymeric resin by the addition of ethylene glycol to a metal complex solution, using citric acid as chelating agent. All the steps of the samples preparation are summarized in the Fig. 1.

Potassium carbonate (Fluka, 99 %) and niobium oxalate (CBMM) were used as precursors of the citrate solution. The polymeric resin was prepared mixing the citrate solution and the ethylene glycol at 90 °C under continuous stirring. The ratios between the cations (K + Nb) and the citric acid and between the citric acid and ethylene glycol were fixed at 3:1 in mols and 40:60 in weight, respectively. The K/Nb molar ratio was varied from 1 to 2. The viscosity of the different coating solutions was adjusted in the range 8 × 10⁻² – 28 × 10⁻² P. The viscosity was adjusted by water addition or evaporation and the values were measured with Brookfield DVII+ Pro viscometer. In this work we used two types of substrates, the so-called standard (non-polished) and polished sintered Al₂O₃, with dimensions 10 × 10 × 0.635 mm³. The first series of samples were prepared by dip-coating using a home made device. Dipping and withdrawing were carried out at a fixed rate of 0.16 mm s⁻¹. A second series were prepared by spin-coating (Spin Coater model KW-4A Chemat technology), varying the rotation duration from 20 to 40 s and the rotation rate from 3000 to 6000 rpm. The wet films were then submitted to two thermal treatment cycles performed under air: i) 300 °C for 4 h using heating and cooling rate of 5 °C min⁻¹ and ii) 500–750 °C for 1–4 h using heating and cooling rate of 5 °C min⁻¹. In the multi-layered films, the whole process (deposition and heat treatment) was repeated several times in order to increase the film thickness. In the case of powder preparation, the resin was submitted to the same thermal treatment cycle. After the first step of calcination (300 °C for 4 h) the pyrolized polymer was de-aggregated in agate mortar and then submitted to the second calcination step (crystallization step—step ii). The influence of the thermal treatment conditions on the phase formation and on the film microstructure was investigated.

The samples were characterized by X-ray diffraction (XRD), field emission scanning electronic microscopy (FE-SEM) and energy dispersive spectroscopy analyses (EDS). The XRD patterns of powders and films were carried out with a powder diffractometer INEL CPS 120, using Cu Kα₁ radiation (λ=1.5406 Å), fixed incident angle (approxi-

Fig. 1. Flowchart of the samples preparation by Pechini Process.
mately 8°) and a curved position sensitive detector. Due to the probed thickness (around 1 μm), EDS is not always well adapted to analyses of thin films. In fact, variation of results was observed when analyses conditions varied. That is why preliminary tests were performed using Rutherford Back-scattering Spectroscopy (RBS) and the EDS analysis was then calibrated from the RBS spectra performed on some identical thin film samples. The optimal experimental conditions were set at 10 kV as accelerating voltage and 10 nA as beam current, using a Jeol JSM 6400 microscope equipped with a link Oxford analyzer. The samples were previously coated with a thin graphite layer to achieve a good surface conductivity and avoid charge effect. Finally, the SEM observations were carried out in a JSM 6301F Field Emission Scanning Microscope, working at low voltage (9 kV), so no metallization was required for microstructure observation.

3. Results and discussion

3.1. KN powders

In a first step, the synthesis and crystallization conditions of powders were determined using the same type of resin as for thin films, except for the viscosity (for powder preparation the resin viscosity was increased up to $38 \times 10^{-2}$ P by water evaporation). Fig. 2 shows the XRD patterns of KN powders, thermally treated at several temperatures for 1 h (complete thermal treatment is 300 °C, 4 h + 500–750 °C, 1 h).

The KNbO$_3$ phase formation can be observed at 550 °C and, as expected, the temperature increase enhances the crystallization. Single-phased samples were obtained. Only above 700 °C quite small additional peaks merged. Due to their low intensity, it was not possible to identify any secondary phase, but it is probable that at these temperatures K deficient phases start to grow. The results obtained with KN powders guided the study in thin film form.

3.2. Dipped films

3.2.1. Coating solution viscosity

In a first step, the influence of the coating solution viscosity on the dip-coating deposition of KN thin films (Fig. 3) was studied. The viscosity of different coating solutions was fixed at $8 \times 10^{-2}$, $12 \times 10^{-2}$, $17 \times 10^{-2}$, $22 \times 10^{-2}$ and $28 \times 10^{-2}$ P. It is well established that too fluid coating solution produces excessively thin films, whereas too viscous ones produce cracked films [23]. In this work, SEM observations showed that, in the studied range, the increase of the coating solution viscosity leads to more homogeneous crack-free films, presenting well-coated substrate surface. Therefore, in this work, we fixed the coating solution viscosity between $17 \times 10^{-2}$ and $22 \times 10^{-2}$ P, which leads to a thickness in a range 70–150 nm.

3.2.2. Influence of K: Nb ratio

Five different molar ratios between K and Nb were studied ([K/Nb] = 1.00, 1.25, 1.32, 1.50 and 2.00) in order to minimize the presence of secondary phases which can be for instance due to the potassium evaporation [10]. The EDS analyses were performed to several samples treated at 550 °C for 1 or 4 h (samples F1 to F3: 1 h, and F4 to F6: 4 h). The results are shown in Table 1. It can be observed that for samples prepared from the resin with K/Nb ratio = 1.50 and

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**Fig. 2.** XRD patterns of KN powders prepared with [K/Nb]=1.50 and heat treated at several temperatures for 1 h.

**Fig. 3.** FE-SEM images of the films prepared using coating solutions presenting viscosity of (a) $8 \times 10^{-2}$ and (b) $22 \times 10^{-2}$ P and heat treated at 550 °C for 1 h. The 1–2 μm features visible on these photos reflect the substrate surface morphology. Inset shows the surface of bare substrate (same magnification).
2.00 (denoted F4, F5 and F6) an excess of potassium was found after the heat treatment. On the other hand, for the other three resins (K/Nb ratio = 1.0, 1.25 and 1.32, samples denoted F1, F2 and F3, respectively) a deficiency of K was verified. As expected, this deficiency is less strong for resin with the K/Nb ratio = 1.25 and 1.32 than for the resin with the K/Nb ratio = 1.00.

This result suggests that, although single-phased KNbO₃ was obtained, the optimum K/Nb ratio was not reached. Several authors have already reported some difficulties to achieve a stoichiometric K/Nb ratio after calcination [9–11,22]. Some strategies were used in order to avoid this problem, but their results are not always satisfactory. For instance, Chow et al. [11] measured a K/Nb molar ratio ranging from 0.70 to 0.95 in films grown by “ion beam sputtering” and treated between 650 and 700 °C. Moreover, it has to be pointed out that a slight K deficiency could improve the film stability relative to ambient moisture. In fact, it was observed that initial brightness of K enriched films disappears after several weeks in ambient atmosphere. There is a possibility of undesired reactions with water molecules due to an excess of K in the film structure. Another point to keep in mind is that EDS is not a high precision method for thin film analysis, in spite of our efforts to use a calibration process with RBS spectra. So, the EDS results should be considered with some caution.

Resins containing K/Nb ratio = 1.25 and 1.50 were then selected for a detailed study of film preparation. Fig. 4 shows the XRD patterns of the resulting samples prepared with [K/Nb] = 1.50. Patterns of bare substrates were also recorded and revealed that the two non-indexed peaks observed in film patterns, at 27.8° and 36.8°, are substrates derived, even if they are not reported as α-Al₂O₃ peaks. Probably, it is a type of contamination since these peaks are not present for all substrates. The shoulder at 2θ = 43.6° (marked as *, in Fig. 4a and b) originates from the sample holder and appears occasionally due to changes in sample size. Neither K deficient nor K enriched secondary phase was observed. Therefore, it was verified that only single-phased KNbO₃ films are obtained, in a reproducible form, well choosing the preparation conditions. Moreover, the KN films were obtained at lower temperature and shorter time heat treatment compared to literature results [2,6,7]. It is noteworthy, from Fig. 4, that crystallization occurs at 550 °C and that increasing the temperature or duration of thermal treatment only slightly affects crystallization. All these films are strictly randomly oriented as can be clearly seen by comparing the relative intensities in Figs. 2 and 4. This result was expected, because the substrates are polycrystalline. Similar XRD patterns were obtained for films prepared from resins with K/Nb = 1.25.

FE-SEM images are displayed in Fig. 5. The observation of the samples treated at 500 °C showed an amorphous-like structure (Fig. 5a), in agreement with the XRD result. On the other hand, the sample treated at 650 °C showed heterogeneous and discontinuous aspect (Fig. 5b), supporting the conclusion that the optimal temperature range for the KN thin films preparation onto rough substrates is reached between 550 and 600 °C. In this range of temperature, crack-free and continuous films presenting a good substrate coverage and well defined grains can be obtained, as shown in Fig. 5c. Depending on the K/Nb used ratio, the optimized temperature and the duration of the thermal treatment should be chosen.

Table 1. Comparison between K/Nb molar ratio in the coating solution and measured by EDS in the annealed films

<table>
<thead>
<tr>
<th>Sample</th>
<th>K: Nb resin molar ratio</th>
<th>K: Nb molar ratio measured by EDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>1.00</td>
<td>0.5</td>
</tr>
<tr>
<td>F2</td>
<td>1.25</td>
<td>0.8</td>
</tr>
<tr>
<td>F3</td>
<td>1.32</td>
<td>0.8</td>
</tr>
<tr>
<td>F4</td>
<td>1.50</td>
<td>1.2</td>
</tr>
<tr>
<td>F5</td>
<td>1.50</td>
<td>1.2</td>
</tr>
<tr>
<td>F6</td>
<td>2.00</td>
<td>1.2</td>
</tr>
</tbody>
</table>

![Fig. 4. XRD patterns of films prepared with the resin R1 (K/Nb=1.50) and heat treated at: a) different temperatures for 1 h and b) at 550 °C during different times. The peaks marked with (#) and (*) correspond to Al₂O₃ substrates and sample holder, respectively.](image-url)
be different, as suggested in Fig. 5d, corresponding to a resin with $K/Nb = 1.25$ instead of 1.50 for Fig. 5a, b and c.

The samples shown in Fig. 5 were prepared onto standard $Al_2O_3$ substrates. Some experiments were carried out using polished $Al_2O_3$ substrates, and it was verified that the main difference concerns the roughness and consequently the substrate coverage. In fact, no significant difference relative to the film’s phase formation was found but it was observed that using polished surfaces it is possible to increase the thermal treatment temperature without discontinuities’ formation. The polished substrates were used for thickness measurements (see Fig. 7).

3.2.3. Multi-layered dipped films

In order to obtain thicker films, which can be more suitable for future applications, multi-layered samples were

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Fig. 5. FE-SEM images (magnification of 10000 ×) of samples prepared using the $K/Nb$ ratio = 1.50, onto standard $Al_2O_3$ substrates and heat treated at (a) 500 °C/1 h, (b) 650 °C/1 h and (c) 550 °C/4 h (inset corresponds to a magnification of 50000 ×, in order to evidence the grains) and (d) sample prepared using the $K/Nb$ ratio = 1.25, onto standard $Al_2O_3$ substrate and heat treated at 550 °C/1 h.

Fig. 6. FE-SEM images of a) F2 (1 layer) and b) F8 (3 layers) samples, heat treated at 550 °C for 1 h after each layer deposition.

Fig. 7. FE-SEM images of the fractured F7 sample (2 layers), heat treated at 550 °C/1 h: a) cross section and b) 45° tilted observations.
prepared onto polished Al₂O₃ substrates. The same conditions used to prepare sample F2 (see Table 1) were chosen. The complete thermal treatment cycle was performed between each layer deposition.

Improvement of film surface morphology when increasing the number of layers was evidenced by FE-SEM observations, as can be seen in Fig. 6: deposition of three layers instead of one leads to denser films, eliminating the discontinuities. These differences are obviously more remarkable onto polished substrates than onto standard ones, as a consequence of their lower roughness.

The thickness was evaluated from FE-SEM cross section images. It can be observed that, as expected, (see Fig. 7 and Table 2) increasing of the layer’s number increases the film thickness without any degradation in the surface quality. Moreover, it appears that the deposition of subsequent layers leads to denser and more homogeneous films.

Fig. 7a and b refers to a two-layered film. Clearly, the film is very dense and smooth. The homogeneity and the adhesion to the substrate appear very good and there is no visible discontinuity between the two layers. A similar result was previously reported in the example of LiNbO₃ films grown by a multi-step process [18].

### 3.3. Spinned films

In order to evaluate the influence of deposition method, a second series of samples were prepared by spin-coating using the resin in which the K/Nb ratio was kept at 1.50 and the heat treatment conditions fixed at 300 °C/4 h followed by 550 °C/4 h. The effect of the rotation rate and duration on the thin film’s microstructure was investigated. No significant differences between dipped and spinned samples were found from XRD analysis. Moreover, changes in the spinning duration also did not produce any significant effect on the sample’s microstructure. In contrast, increasing the rotation rate leads to remarkable microstructural differences. While the sample prepared at 3000 rpm shows the smoothest microstructure, similar to the dipped samples, the ones prepared at higher rotation have a less homogeneous aspect, presenting striated structures. The high roughness of the standard alumina substrates did not allow to perform the thickness measurements, but the observed striated structures can be ascribed to a limited substrate coating, as these structures are substrate derived (bare substrates also show these striated structures). In this context, it can be concluded that best results onto standard Al₂O₃ substrates are achieved when the samples were prepared at 3000 rpm, for rotation duration in the range 20–40 s.

### 4. Conclusions

Homogeneous and single-phased KN powders and thin films on sintered alumina substrates were successfully prepared using the easy processing and low-cost Pechini method. Crystalline and crack-free samples, with good substrate coverage and good adhesion were achieved using both experimented deposition methods, dip- and spin-coating, by adjusting the deposition and calcination parameters. The crystallization of the KNaO₃ phase starts at 550 °C. The deposition of single layer produces films presenting a thickness around 100 nm. Moreover, the deposition of subsequent layers allows to increase the film thickness (around 100 nm for each step) without any surface quality degradation. On the contrary, the multilayers lead to denser and smoother samples. Among all studied parameters, the only one we could not adjust accurately was the K/Nb ratio in the final sample. Even testing several composition in the starting solution and varying the thermal treatment conditions, a deviation of about 20% in the K/Nb ratio was always found from EDS analysis. Further efforts are being carried out to improve the composition in order to study, in next steps, precisely the influence of composition on physical behavior of thin films. In fact, it has to be pointed out that in literature, generally, single-phase type XRD pattern is the criteria of identification of KNbO₃ films.

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