

# Preparation of potassium tantalate niobate thin films by chemical solution deposition and their characterization

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## Abstract

Potassium tantalum niobate ( $\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$ , (KTN), where  $x = 0, 0.21, 0.36, 0.53, 0.74, 0.82, 0.86,$  and  $1$ ) thin films of perovskite structure were prepared by chemical solution deposition on Si and  $\text{SiO}_2$  glass substrates. A homogeneous and stable precursor solution was obtained by dissolving potassium, niobium and tantalum isobutoxides in absolute isobutanol and an addition of diethanolamine as a modifier. Optimum conditions for film preparation were found. Annealing temperature and heating regime,  $\text{Al}_2\text{O}_3$  “chemical” buffer layer and  $\text{KNbO}_3$  seeding layer were the determining factors for film quality. It was demonstrated by X-ray diffraction that the films have desired pseudocubic perovskite structure. Infrared transmittance was measured for broad range of Ta/Nb ratios. The spectra show continuous transformation from  $\text{KTaO}_3$  to  $\text{KNbO}_3$  and indicate that the optical axis lies in the plane of the film.

*Keywords:* thin films, tantalates niobates, chemical solution deposition, infrared spectroscopy

## 1. INTRODUCTION

Potassium tantalate niobate,  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  (KTN), thin films have received a great deal of attention owing to their piezoelectric, pyroelectric, and electrooptic properties. As only KTN films with perovskite structure have these desirable properties, therefore the formation of pyrochlore phase should be avoided at their preparation. The paraelectric cubic perovskite phase of KTN (Ta/Nb = 65/35) is the most frequently studied because it is a promising candidate material for IR detectors and electro-optic devices thanks to its very large quadratic electrooptic coefficient and photorefractive effect <sup>1</sup>. Using different procedures including chemical solution deposition (CSD) method, KTN perovskite thin films have been

successfully prepared<sup>1,2,3,4</sup>. Highly (100)<uvw> oriented KTN(65/35) perovskite films<sup>1</sup> were prepared from alkoxide precursors deposited on (100)SrTiO<sub>3</sub>, and (100)MgO and annealed at 700°C, and 750°C, respectively. Quite similar films<sup>2</sup> were also prepared from hydrolysed alkoxide sols deposited on (100)MgO and annealed at 700°C, unfortunately, only pyrochlore phase was detected in KTN(65/35) films<sup>2</sup> deposited on (100)Si, (1-102)Al<sub>2</sub>O<sub>3</sub> and (01-10)SiO<sub>2</sub>. Besides, various substrate types<sup>3</sup> were tested for KTN(65/35) film preparation. In addition to the substrates mentioned above, also Pt-coated (111)Si, (100)YSZ, (110)SrTiO<sub>3</sub>, and (012)LaAlO<sub>3</sub> were used. It was concluded<sup>3</sup> that the phase composition of the KTN thin films had a strong dependence on the crystal structure of the substrates, while other processing parameters (chemical additives to sol, annealing regimes) played less important roles. Using substrates (100) and (110)SrTiO<sub>3</sub>, and (100)MgO with lattice parameters and crystal symmetry close to KTN, the pure perovskite phase was obtained. The KTN films contained a varying portion of pyrochlore phase on the substrates which exhibited lower degree of crystallographic matching ((100)YSZ, (1-102)Al<sub>2</sub>O<sub>3</sub>, (012)LaAlO<sub>3</sub>). Only the pyrochlore phase was observed on the substrates having no structural similarity with the film (amorphous SiO<sub>2</sub> and Pt-coated (111)Si). The structural, dielectric, and ferroelectric properties of a series of KTN thin films with compositions (65/35, 50/50, and 35/65), and deposited on bare and Pt-coated (100)MgO were studied<sup>4</sup>. Pure perovskite phase was grown on both types of substrates at 700°C with a high degree of preferred (100) orientation. In summary, in all above mentioned papers the maximum content of Ta in KTN films reached 65%, and preparation of pure perovskite phase was successful only when a crystallographically similar single crystal substrate (i.e., SrTiO<sub>3</sub> or MgO) was used.

This paper describes the preparation of a series of KTN perovskite thin films, covering the entire interval of Ta:Nb ratios, deposited on (100)Si, and SiO<sub>2</sub> glass substrates.

## 2. EXPERIMENTAL

Ta(OCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>)<sub>5</sub>, Nb(OCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>)<sub>5</sub>, and K(OCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>) were chosen as starting compounds for the synthesis of KTaO<sub>3</sub> (KT) and KNbO<sub>3</sub> (KN) sols, together with absolute HOCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub> as a solvent, and 2,2-diethanolamine as a modifier. Detailed procedures of precursor syntheses, their handling, and substrate cleaning are given elsewhere<sup>5</sup>. In order to minimize the loss of potassium due to the evaporation and reaction with the underlying layers, 5-7% excess of potassium in KTN sols with respect to stoichiometric concentration was used. Al(OCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub> with absolute (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>OH

as the solvent, and 2,2-diethanolamine as a modifier were used for the preparation of the sol for Al<sub>2</sub>O<sub>3</sub> buffer layer deposition (see our previous paper<sup>5</sup>). Unhydrolysed solutions were deposited by spin – coating (Karl Suss Gyrset coater) at 2000 rpm. After their deposition the samples were dried (at 110°C for 5 min) in a drying chamber, and then pyrolysed in a preheated furnace. If necessary, the deposition - drying - pyrolysis cycle was repeated until the desired thickness was reached. Finally, the samples were crystallized by annealing. The conditions for the pyrolysis and annealing steps were different depending on the type of the deposited layer: the Al<sub>2</sub>O<sub>3</sub> buffer layer was pyrolysed at 450°C for 5 min, and annealed at 800°C for 60 min; the KTN layers were pyrolysed at 550°C for 5-10 minutes. The annealing was carried out under the conditions simulating the rapid thermal annealing technique: the pyrolysed sample was immersed quickly into the muffle furnace preheated at 750°C and annealed for 5 minutes. The composition of KTN sols and films was determined by means of the volumetric titration and electron microprobe analysis, respectively. The thickness of films was measured by a stylus profilometer, the crystallization behavior was determined mainly by powder X-ray diffraction (XRD) and atomic force microscopy (AFM). Further characterization of the perovskite films was done using far infrared spectra. The infrared transmittance on KTN thin films was measured in the spectral range from 30 to 700 cm<sup>-1</sup> at room temperature using a Bruker IFS 113v Fourier transform spectrometer. The raw experimental spectra show interference fringes originating in multiple passage of infrared radiation in the Si substrate. The fringes were eliminated by a Fourier-transform filtering of the transmittance.

### 3. RESULTS AND DISCUSSION

#### *Preparation*

This work is a continuation of our previous study<sup>5</sup> dealing with the preparation of KTaO<sub>3</sub> (KT) perovskite thin films. It was confirmed that the parameters which are optimal for the preparation of pure KT layers<sup>5</sup> are suitable also for the preparation of KTN layers with various Ta/Nb ratio.

Concerning the formation of perovskite phase in thin films, two main issues seem to be decisive. The first one is the stability of perovskite phase at higher temperatures and of pyrochlore phase at lower temperatures. The second one is the high volatility and reactivity of basic potassium towards the acidic substrates. There is a temperature range from 750 to 850°C and time of a few (2 to 12) minutes, in which the perovskite phase is formed in KTN films preferentially. It can be seen from X-ray patterns of KTN films annealed at various

temperatures presented in Fig. 1. Below the lower temperature limit a pyrochlore phase crystallizes preferentially, above the upper limit the formation of potassium deficit phases as  $K_6Ta_{10.9}O_{30}$  is inevitable.

An  $Al_2O_3$  film of thickness above 200 nm is used to separate the substrate from the deposited film chemically (“chemical” buffer layer). This substantially reduces the loss of potassium due to its reaction with acidic substrates as Si and  $SiO_2$  glass. A pseudocubic KN layer (thickness 60 nm, lattice misfit  $< 2\%$  in comparison with pure KT) was used as a seeding layer to promote the growth of perovskite KTN films via the grain growth from seed islands.

### ***Characterization***

The series of powder X-ray patterns for KTN films with various Ta/Nb ratio is shown in Fig. 2. The plotted X-ray data look similarly and confirm the perovskite-like structure of the KTN films for all Ta/Nb ratios. The diffraction peaks are not split even in the Nb-rich samples (note that bulk  $KTaO_3$  is cubic but  $KNbO_3$  is orthorhombic at room temperature). This indicates a pseudocubic symmetry of our films which could be explained by their nanocrystalline character. It is well known that the deviation from the cubic phase is quite reduced for such small crystallites. It is well known that the deviation from the cubic phase is quite reduced for such small crystallites<sup>6</sup>.

The transmittance spectra for varying Ta/Nb ratio are displayed in Fig. 3. KT keeps the cubic crystal structure over the entire temperature range and its spectrum shows the characteristic patterns for perovskites. It consists of three minima corresponding to the frequencies of the optically active transverse phonons, which can be assigned to  $F_{1u}$  reducible representations of the group theory. They are located<sup>7</sup> at the frequencies 90, 200 and  $550\text{ cm}^{-1}$ . The crystal structure of KN at room temperature is orthorhombic with the crystal axes  $a \approx c$ . Its polarized infrared spectra are generally different along the particular crystal axes. They can be classified<sup>8</sup> by  $A_1$ ,  $B_1$  and  $B_2$  representations in orthorhombic and  $A_1$  and E in pseudocubic structure. In the latter case, the phonon frequencies are at 60, 198 and  $516\text{ cm}^{-1}$  for the E symmetry and at 190, 295 and  $600\text{ cm}^{-1}$  for the  $A_1$  symmetry.

The positions of the phonons in Fig. 3 are in reasonable agreement with the data on bulk materials. On contrary to X-ray diffraction, which shows pseudocubic character, infrared spectra of KN display features of strong uniaxial material. We measured unpolarized spectra because our films are polycrystalline, therefore our infrared spectra are superposition of the spectra parallel and perpendicular to optical axis. The continuous transformation from the KT to KN spectrum can be clearly observed with varying Ta/Nb ratio. In the KN spectrum, the  $A_1$

component is quite enhanced. It indicates that the crystallites prefer the orientation with the optical axis in the film plane. The absolute values of the transmittance depend on the film thickness and its homogeneity. These parameters vary for our films, so we cannot compare them. The position of the minimum is, however, independent of them.

#### 4. CONCLUSIONS

A CSD method was used to prepare polycrystalline  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  films on different substrates in the entire range of Ta/Nb ratio. The conditions of their preparation were optimized. It was demonstrated by X-ray diffraction that the films have pseudocubic perovskite structure. Infrared transmittance was measured for eight different Ta/Nb ratios. The spectra show continuous transformation from KT to KN and indicate that the optical axis lies in the plane of the film.

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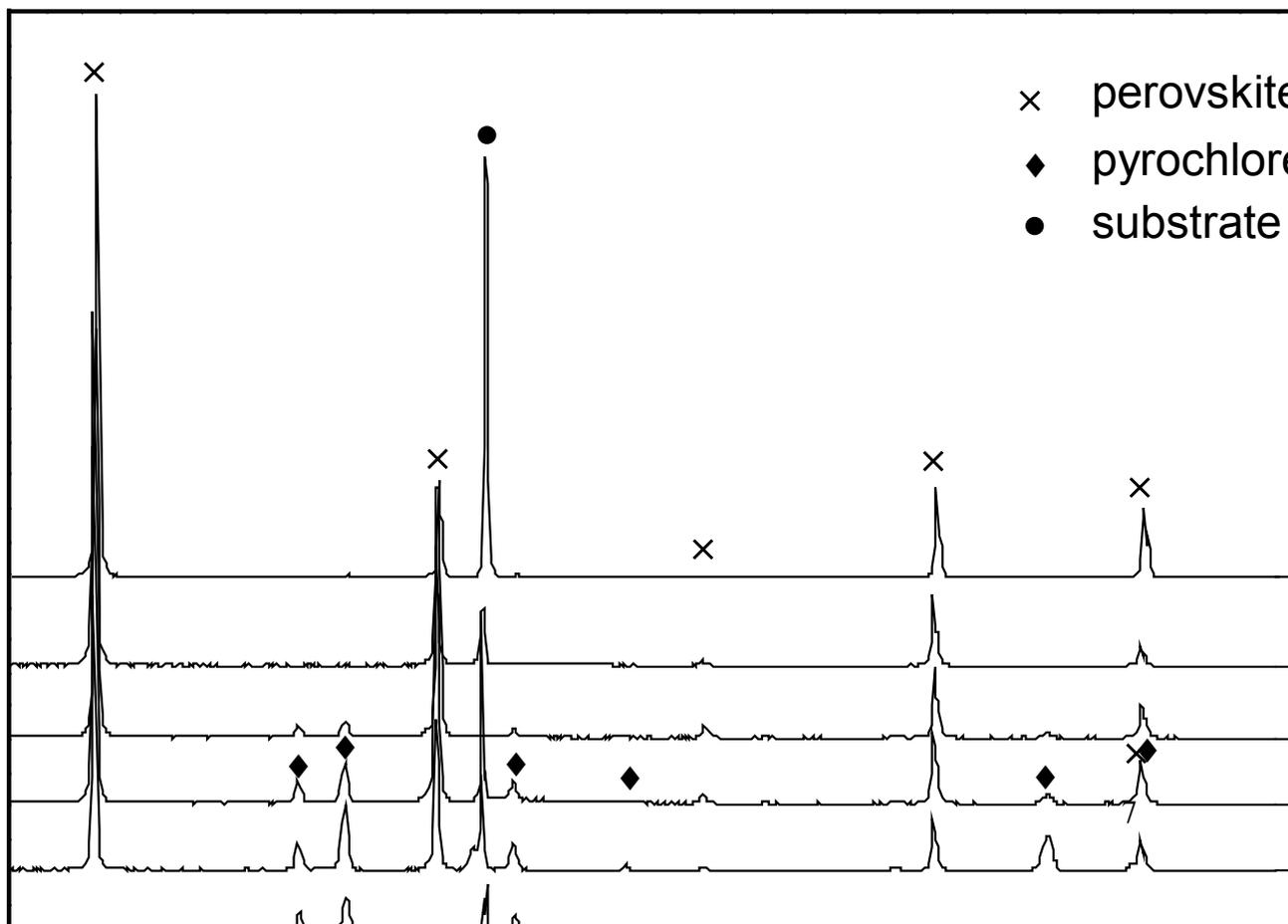
## FIGURE CAPTIONS

Fig. 1. XRD patterns of KTN films on SiO<sub>2</sub> glass substrate, with Al<sub>2</sub>O<sub>3</sub> and KN buffer layers, heat-treated at different temperatures under heating regime simulating rapid thermal annealing technique.

Fig. 2. X-ray diffractograms of KTN films with varying Ta/Nb ratio. Films were deposited on Si and SiO<sub>2</sub> substrates at optimized conditions.

Fig. 3. Concentration dependence of far infrared transmittance spectra on KTN thin films deposited on (100)Si substrate with Al<sub>2</sub>O<sub>3</sub> buffer layer and KNbO<sub>3</sub> seeding layer.

Fig. 1



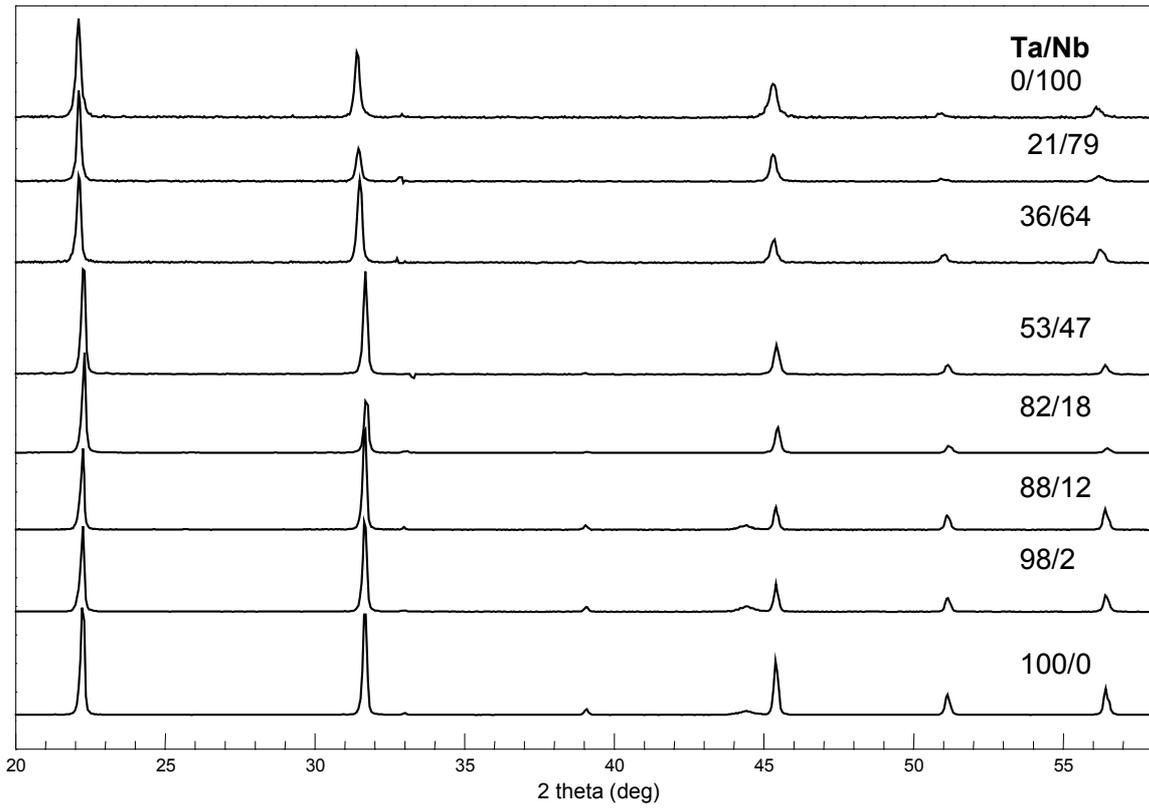


Fig. 2

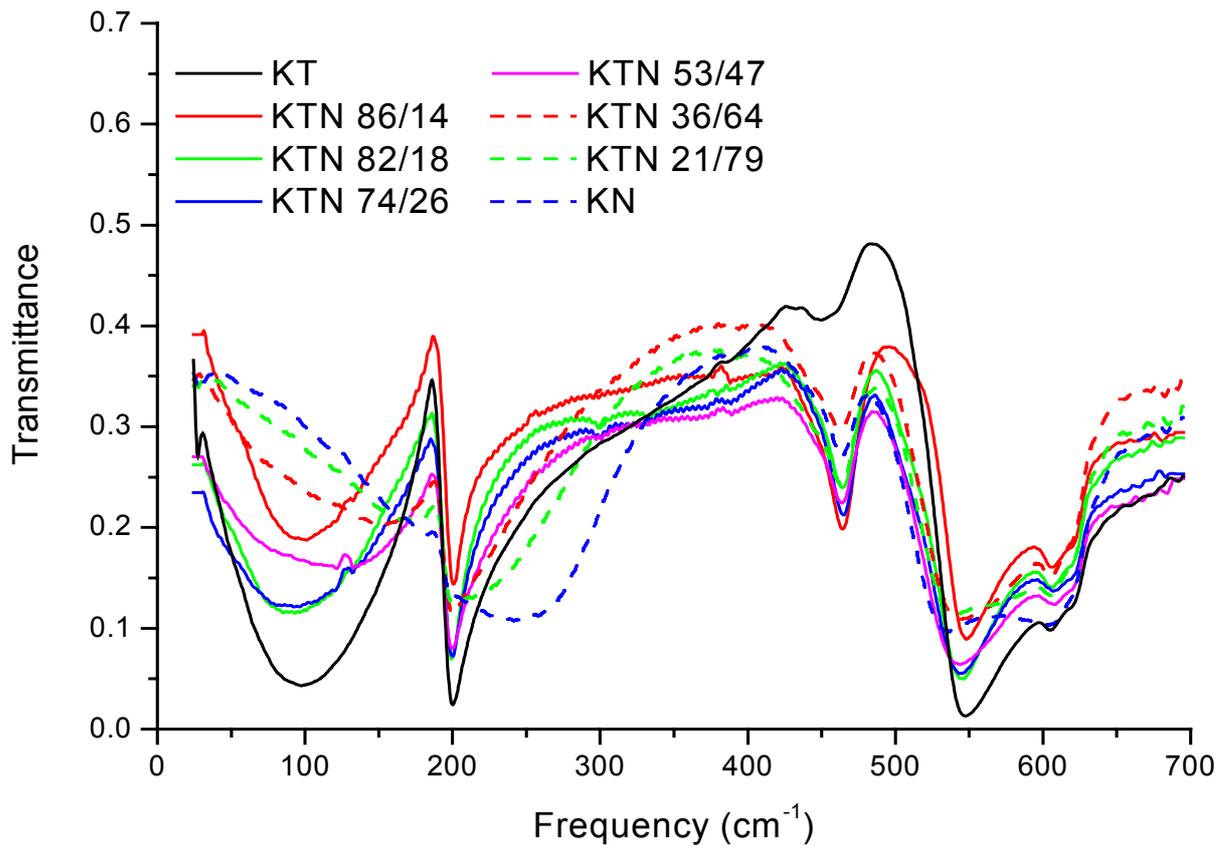


Fig. 3