# Growth of epitaxial films of sodium potassium tantalate and niobate on single-crystal lanthanum aluminate [100] substrates

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Epitaxial films of sodium potassium tantalate ($Na_{0.5}K_{0.5}TaO_3$, NKT) and sodium potassium niobate ($Na_{0.5}K_{0.5}NbO_3$, NKN) were grown on single-crystal lanthanum aluminate (LAO) (100) (indexed as a pseudo-cubic unit cell) substrates via an all-alkoxide solution (methoxyethoxide complexes in 2-methoxyethanol) deposition route for the first time. X-ray diffraction studies indicated that the onset of crystallization in powders formed from hydrolyzed gel samples was 550 °C. $^{13}C$ nuclear magnetic resonance studies of solutions of methoxyethoxide complexes indicated that mixed-metal species were formed, consistent with the low crystallization temperatures observed. Thermal gravimetric analysis with simultaneous mass spectrometry showed the facile loss of the ligand (methoxyethoxide) at temperatures below 400 °C. Crystalline films were obtained at temperatures as low as 650 °C when annealed in air. θ-2θ x-ray diffraction patterns revealed that the films possessed c-axis alignment in that only (*h*00) reflections were observed. Pole-figures about the NKT or NKN (220) reflection indicated a single in-plane, cube-on-cube epitaxy. The quality of the films was estimated via ω (out-of-plane) and φ (in-plane) scans and full-widths at half-maximum (FWHMs) were found to be reasonably narrow (~1°), considering the lattice mismatch between the films and the substrate.

## I. INTRODUCTION

Sodium potassium niobate ($Na_{0.5}K_{0.5}NbO_3$, NKN) is a lead-free perovskite ferroelectric material with a number of technologically useful properties. Dielectric constants as high as 580 at a thickness of 650 nm have been reported in thin films,[1] and a remnant polarization of 23.5 μC/cm$^2$ has been reported.[2] Blomqvist et al.[3] have demonstrated optical waveguides in films of NKN on single-crystal aluminum oxide. Good-quality epitaxial thin films minimize scattering losses, resulting in an increase in light transmission. [Wave-guiding efficiency decreases due to the scattering losses at sites of imperfection within the wave guiding film such as grain boundaries, film top surfaces, crystalline defects, and the film–substrate interface. For efficient and compact thin-film waveguides, it is also necessary that (i) the refractive index of the substrate to be lower than that of the electro-optic film, (ii) the film is appropriately thick to allow for the transport of photons of various energies (significant fraction of the wave length of light), and (iii) for compact devices, the difference between film and substrate refractive indices is as large as possible.]

The reported optical properties of NKN[4] indicate thin films of NKN appear to be a viable alternative to the prototypical ferroelectric waveguide materials barium titanate or lead zirconium titanate when prepared as an epitaxial thin film. When deposited by chemical methods

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(chemical vapor deposition, sol-gel, or metal-organic deposition), barium precursors frequently form thermally stable barium carbonate intermediate phases that may require temperatures above 800 °C to crystallize the desired film.[5] Lead zirconium titanate deposited by chemical means generally must be heated above 700 °C to convert from a metastable pyrochlore phase into the desired perovskite phase.[6]

Previous studies of epitaxial films of NKN have used magnetron sputtering[1–4] or laser ablation[7] as the film deposition technique. As an alternative to vacuum processing, we have used a new solution deposition technique involving the sol-gel chemistry of metal methoxyethoxides in 2-methoxyethanol. Solution deposition requires no vacuum equipment and no target preparation, gives accurate and reproducible control over stoichiometry, and separates the low temperature film casting step from the high-temperature annealing step, thus giving great flexibility in thermal processing.[6] Of particular utility are methoxyethoxide complexes in 2-methoxyethanol because of the high solubility and wide application of this chemistry to a number of elements.[8] We have previously reported on the growth of epitaxial oxide thin films on both single-crystal oxide[9] and roll-textured metal substrate.[10]

The deposition of polycrystalline films of NKN on oxidized silicon using methoxyethoxides has been reported,[11] but to our knowledge, there are no reports of epitaxial growth from solution methods. In this paper, we describe the development of an all-alkoxide solution deposition route starting with solution studies of the precursor solutions, thermal studies of gel decomposition, structural studies as a function of temperature of powder formation, and structural studies of epitaxial thin film growth on single-crystal (100) lanthanum aluminate (LAO). Finally, exploiting the simplicity and flexibility of solution deposition, we describe the epitaxial deposition of the less-studied tantalate derivative, sodium potassium tantalate ($Na_{0.5}K_{0.5}TaO_3$, NKT).

## II. EXPERIMENTAL

All reactions were performed under an inert atmosphere using standard Schlenk techniques. Starting materials were stored, weighed, and transferred in an inert atmosphere dry-box. Sodium metal, potassium metal, tantalum (V) ethoxide, niobium (V) ethoxide, and 2-methoxyethanol (anhydrous, >0.005% water) were used as received.

### A. Precursor solution synthesis

Solutions (1.0 m) of sodium and potassium methoxyethoxide were prepared by the direct reaction of sodium metal and potassium with 2-methoxyethanol, respectively. Solutions (1.0 m) of tantalum and niobium methoxyethoxide were prepared via exchange of the ethoxide ligand for methoxyethoxide by reaction in excess 2-methoxyethanol. The resulting solutions were allowed to reflux for 1 h, and half the solution was removed by distillation at atmospheric pressure. Following redilution to the original volume, this process was repeated twice more to ensure that complete ligand exchange had occurred, and this was verified by $^{13}C$ solution nuclear magnetic resonance (NMR). Stoichiometric aliquots of the three solutions were prepared gravimetrically and mixed, allowing for the preparation of 0.5 M precursor solution. For the experiments described in this work, no excess alkali was used.

### B. NMR measurements

Solutions for $^{13}C$ NMR were prepared by charging a 5-mm-diameter NMR tube with 1 $cm^3$ 0.5 M solution of each of the individual methoxyethoxides and of the mixtures. The sample tube was connected to a high vacuum line, and the excess 2-methoxyethanol was distilled at ~35 °C over a period of 1 h, resulting in a viscous oily residue occupying approximately 20% of the initial volume. Deuterated benzene was distilled into the tube to restore the solution level to the initial volume, and the entire residue dissolved. Proton decoupled $^{13}C$ spectra were obtained at 23 °C using a frequency of 75 MHz.

### C. Thermogravimetric analyzer (TGA)/ gas analysis

Thermogravimetric analyses were performed on gels of Na, K, Ta, Nb, NKT, and NKN. Thermogravimetric data were obtained using a TA Instruments TGA 2950 (New Castle, DE). This instrument is interfaced to a Balzers Thermostar (Nashua, NH) mass spectrometer (0–100 amu, equipped with electron multiplier) through a capillary tube. Samples were prepared by hydrolysis of coating solutions with a slight excess of water in 2-methoxyethanol, followed by vacuum drying for 30 min at 90 °C. Samples (20–40 mg) were place in a tared platinum sample holder. The TGA was ramped from ambient temperature to 1000 °C at a ramp rate of 20 °C/min in an atmosphere of 20% $O_2$ and 80% Ar. Starting at 200 °C, mass spectra of the entire mass range (0 to 100) were obtained every 50 s.

### D. XRD studies of powder samples

Powder samples were obtained from hydrolyzed precursor solutions. Precursor solutions (0.5 M) were mixed with a 3-fold excess of water in 2-methoxyethanol and heated to 35 °C under stirring on a hot plate. After about 25 min, a transparent gel formed. The gel was dried at 150 °C, crushed, and fired in air at temperatures ranging from 500 to 900 °C for 1 h.

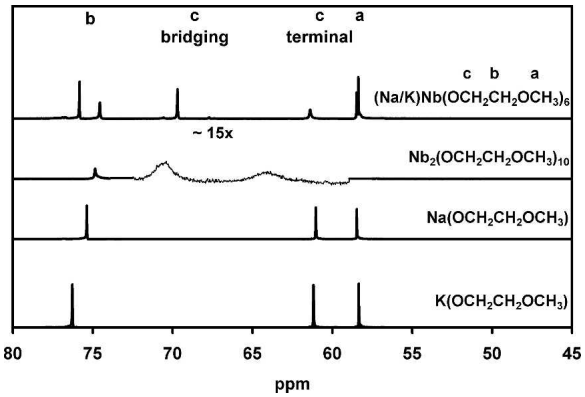


FIG. 1. $^{13}$C NMR spectra of K, Na, Nb, and NKN 2-methoxyethoxides.

### E. Film deposition and crystallization

Lanthanum aluminate substrates, 1.0 × 1.0 × 0.1 cm, were ultrasonically cleaned in toluene followed by isopropanol and heat treated at 1000 °C for 1 h. NKT and NKN films were deposited from 0.5-M stock solution filtered through a 0.2-μm syringe filter by spin-casting at 3500 rpm for 30 s. Solutions were not prehydrolyzed as we have not found it necessary to obtain good coating on oxide substrates. By not prehydrolyzing the solutions, we can reproducibly deposit uniform films of consistent thickness over a period of more than 30 days from a stock solution. In addition, excess hydrolysis promotes crystallization in the bulk of the film rather than templated growth from the interface, leading to degradation of epitaxy.[12] Following deposition, the films were annealed in air in a preheated muffle furnace at temperatures ranging from 500 to 900 °C for 1 h. The best results in terms of crystallinity and minimal surface roughness were obtained at 700 °C. The thickness of one layer films was determined by ellipsometry to be 50 ± 2 nm. Thicker films were built up through multiple coating and firing cycles.

## III. DISCUSSION

$^{13}$C NMR investigations were performed on the solutions used to synthesize powders and thin films of NKT and NKN. Relative little previous work has been done on NMR spectroscopy methoxyethoxide precursors. Kato et al.[13] and Thomas et al.[14] have studied methoxyethoxide precursor solutions of strontium bismuth niobate (SBN) and tantalate (SBT), and Caruso et al.[15] have studied precursors of lead zirconium titanate (PZT). Figure 1 shows the $^{13}$C spectra of sodium, potassium, niobium, and sodium potassium niobium methoxyethoxides (spectra for tantalum containing complexes are similar). Table I reports the resonances observed for the alkoxide compounds. The resonances of the methoxy methyl carbon (carbon a) were observed between approximately 58 and 59 ppm for all of the spectra. The chemical shifts of these resonances were relatively insensitive to cationic environment. The resonances of the methylene carbon adjacent to the methoxy methyl group (carbon b) were observed between approximately 74 and 76 ppm for all of the spectra. As with carbon a, the chemical shifts of these resonances were also relatively insensitive to cationic environment. The resonances of the alpha carbon (carbon c) were observed between approximately 61 and 72 ppm and were sensitive to the cationic environment and provided the most information on structure.

### A. Sodium and potassium methoxyethoxides

Spectra collected for these samples were similar and consisted of the expected three carbon resonances. When the sodium and potassium methoxyethoxides were mixed, six resonances were observed at the chemical shift values of the individual alkoxides, indicating little or no interaction (complex formation or exchange).

### B. Tantalum and niobium methoxyethoxides

Spectra collected for these samples were similar and showed four carbon resonances. The presence of two weak and broad c carbon resonances indicated the presence of terminal and bridging alkoxides that undergo ligand exchange on the NMR timescale. The tantalum and niobium methoxyethoxides most likely undergo dimerization to form complexes of $Ta_2(OCH_2CH_2OCH_3)_{10}$ and $Nb_2(OCH_2CH_2OCH_3)_{10}$ (two bridging alkoxides are present within each complex) as shown in Fig. 2. Many primary Ta and Nb alkoxides are dimers as it provides

TABLE I. $^{13}$C NMR resonances [parts per million relative to tetramethylsilane (TMS)] of Na, K, Ta, Nb, NKT, and NKN methoxyethoxides.

| Metal alkoxides | Methoxy methyl resonances | Methylene carbon adjacent to the methoxy group | Methylene carbon attached to the ethoxide oxygen (terminal ligand) | Methylene carbon attached to the ethoxide oxygen (bridging ligand) |
|---|---|---|---|---|
| $Na(OCH_2CH_2OCH_3)$ | 58.47 | 75.37 | 61.04 | ... |
| $K(OCH_2CH_2OCH_3)$ | 58.34 | 76.27 | 61.18 | ... |
| $Ta_2(OCH_2CH_2OCH_3)_{10}$ | 58.62 | 74.85 | 64.89 | 70.95 |
| $Nb_2(OCH_2CH_2OCH_3)_{10}$ | 58.58 | 74.74 | 64.21 | 71.18 |
| Double alkoxides | | | | |
| $Na_{.5}K_{.5}Ta(OCH_2CH_2OCH_3)_6$ | 58.40 and 58.48 | 76.19 and 74.56 | 61.43 | 68.47 |
| $Na_{.5}K_{.5}Nb(OCH_2CH_2OCH_3)_6$ | 58.47 and 58.37 | 75.83 and 74.55 | 61.389 | 69.69 |

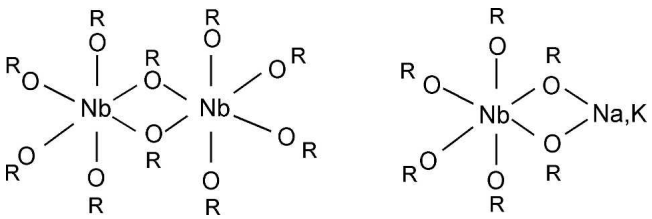


FIG. 2. Proposed structures of methoxyethoxide compounds of niobium and sodium, potassium, and niobium (R $= -CH_2CH_2OCH_3$).

each metal atom with octahedral coordination.[16] This exchange was observed by us in our study[14] of SBT and SBN but was not reported by Kato et al.[13] In the spectrum of the zirconium methoxyethoxide dimer reported by Caruso et al.,[15] the c carbon resonances are also split into bridging and terminal resonances while the a and b resonances are not split.

### C. Sodium potassium tantalum and sodium potassium niobium methoxyethoxides

Spectra collected for these samples were similar and showed the presence of six carbon resonances each. The NMR spectra of the NKT and NKN methoxyethoxides consisted of resonances (with slightly different chemical shifts) that resemble a combination of the Na/K spectra with the spectra of the appropriate transition metal. However, the resonances of the axial and the bridging resonances of the c carbon observed in the Ta and Nb spectra are no longer observed. Instead, the peaks have coalesced, and only a single Ta or Nb c carbon resonance is observed. This most likely means that a double alkoxide exists in solution. The double alkoxide that forms possesses a structure in which two alkoxide ligands bridge the Na/K and Ta or Nb sites resulting in a six-coordinate Ta or Nb site and a two-coordinate Na/K site. The c carbon resonances located at approximately 68 ppm for both systems are respectively attributed to the c carbon of the two bridging ligands. The c carbon resonances located at approximately 61 ppm for both systems are attributed to the axial and planar methoxyethoxide ligands attached to the respective transition metal. The presence of a single resonance for this site and the sharpness of all lines indicate that the axial and planar ligands do not exchange on the NMR time scale. Figure 2 depicts a structure consistent with the observed NMR spectra. We[14] and others[13] have previously observed similar behavior in a study of the $^{13}C$ NMR spectra of methoxyethoxide precursors of $SrBi_2Nb_2O_9$ in that the reaction of Nb methoxyethoxide and Sr methoxyethoxide resulted in a nonfluxional bridged compound of composition $SrNb_2(OCH_2CH_2OCH_3)_{12}$.

### D. Thermal analysis

Thermogravimetric analyses of niobium and tantalum gels prepared by the hydrolysis of methoxyethoxide solutions showed that the materials reached constant weight at ~400 °C and were stable to above 1000 °C. In contrast, the sodium and potassium gels were not completely decomposed until 550 °C and then lost weight above 700 °C. In a previous study of lithium niobate formation by sol gel chemistry, Payne et al.[17] observed that niobium gels decomposed to the oxide while lithium decomposed to a carbonate or oxycarbonate before forming an oxide that was volatile at higher temperatures, in good agreement with our results using sodium and potassium. The thermogravimetric analyses of NKN and NKT are shown in Figs. 3 and 4, respectively. Three distinct weight loss regions are observed: below 200 °C, 200–400 °C, and 500–650 °C. To further study the thermal behavior of these materials, an analysis of the gases evolved during thermal processing was undertaken.

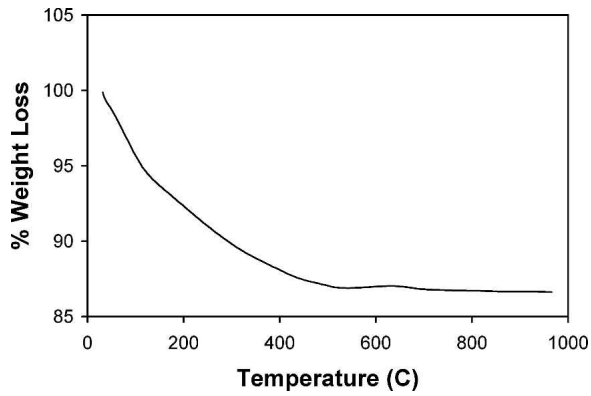


FIG. 3. Thermal gravimetric analysis of NKN gel.

### E. Gas analysis

Mass spectrometric analyses were performed on the gases evolved during the heat treatment of powders of the individual precursor gels and on the mixed cation gels. For the Ta and Nb gels, only water and 2-methoxyethanol were observed, while the Na, K, NKT, and NKN species also evolved carbon dioxide at higher temperatures. Figure 5 shows the temperature dependent

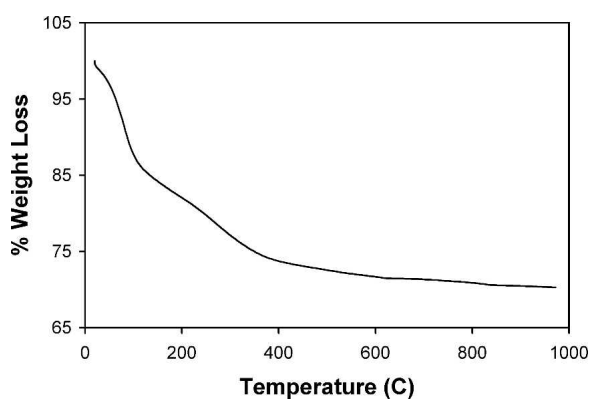


FIG. 4. Thermal gravimetric analysis of NKT gel.

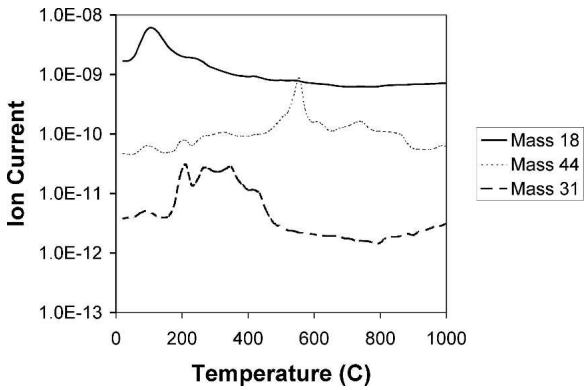


FIG. 5. Mass spectrometric analysis of NKT gel off-gasses (amu 18, 31, and 44 are respectively $H_2O$, $H_3CO^+$, and $CO_2$).

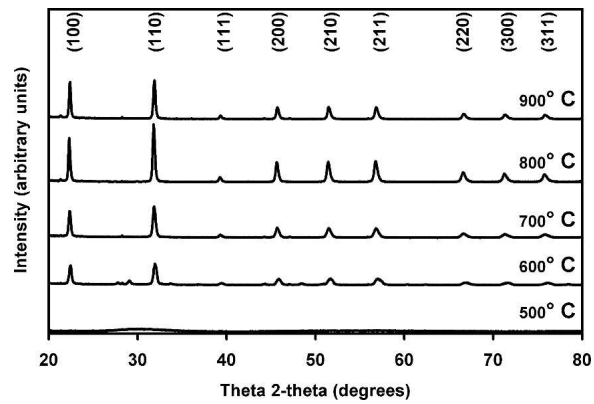


FIG. 6. θ-2θ x-ray diffraction patterns of powders of NKT heat treated from 500 to 900 °C. (Background has not been removed.)

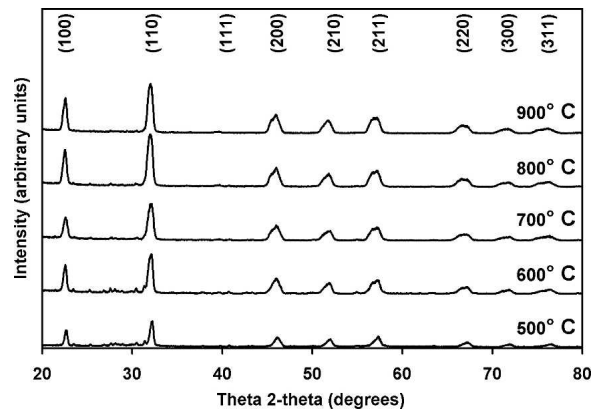


FIG. 7. θ-2θ x-ray diffraction patterns of powders of NKN heat treated from 500 to 900 °C. (Background has not been removed.)

evolution of water [mass to electron charge (m/e) 18], 2-methoxyethanol (m/e 31, $-OCH_3$), and carbon dioxide (m/e 44) for the thermal treatment of an NKT gel. Below 200 °C, the major process is coupling of hydroxyl groups to form metal oxides and release water. Between 200 and 400 °C, the major process appears to be the coupling of hydroxyl and methoxyethoxide ligand to form metal oxides and release 2-methoxyethanol. The cracking patterns observed in this temperature range indicate that only water and 2-methoxyethanol are present in the evolved gas, with no obvious indication of ligand decomposition. Between 500 and 600 °C, metal carbonates and oxycarbonates decompose to metal oxide and carbon dioxide. The source of this carbonate formation may be the decomposition of the ligand to form carbonates or oxycarbonates, or they may be formed as a result of reaction of carbon dioxide (presumably from ligand decomposition) with the alkali oxides. Evidence for the latter is that the NKN sample (Fig. 3) actually gains mass between 600 and 650 °C. This was observed for several samples. (Although the measurements were performed in an inert gas, the flow out of the TGA cell is very low.)

## F. Powder characterization

Powders of NKT (Fig. 6) and NKN (Fig. 7) formed by the heat treatment of precursor gels were characterized using x-ray diffraction. The NKT sample was amorphous at 500 °C, and crystallization occurred at approximately 550 °C. Crystallinity improved with increasing temperature to 800 °C, with the average grain size increasing from 18 nm at 600 °C to 35 nm at 800 °C based on the width of the deconvoluted (110) peaks. The peaks of the 900 °C sample were significantly less intense than those of the 800 °C sample, consistent with some decomposition of the compound at these temperatures and supported by the gradual weight loss observed in TGA (Fig. 3). In contrast, the NKN sample appears to crystallize at slightly lower temperatures and is more stable at higher temperatures. The onset of crystallization is 500 °C; crystallinity improves only slightly (average grain size 20 nm) with increasing temperature to 800 °C, and the 900 °C sample is unchanged from the 800 °C sample. The TGA of NKN (Fig. 2) shows no weight change from 700 to 900 °C. Finally, the NKN sample shows the expected orthorhombic splitting of the higher angle peaks, while the NKT sample does not.

## G. Film characterization

θ-2θ x-ray diffraction patterns revealed sharp, intense, [*h*00] reflections, indicating that the films possessed a high degree of c-axis alignment. Figure 8 shows representative diffraction patterns for three-layer (1500-Å-thick) NKN and NKT films, and Table II reports the calculated lattice constants and full width at half-maximum (FWHM) of the (100) rocking curves (ω-scans) for NKN and NKT on LAO. The sharpness of the FWHMs of the rocking curves is comparable to that reported for sputtered films of NKN on LAO and is indicative of good crystallinity. To assess the degree of in-plane orientation, pole figures and ϕ scans about the (220) reflection were obtained. The pole figures showed the expected 4-fold symmetry and revealed a simple

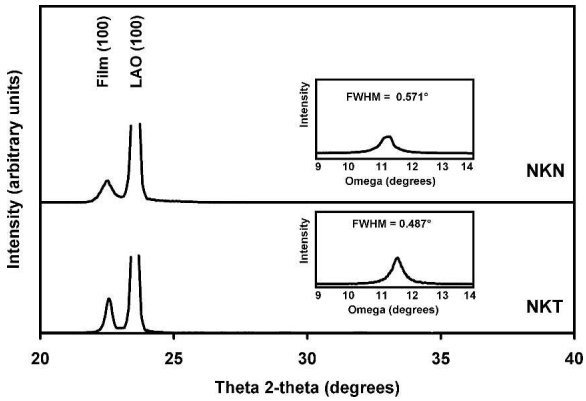


FIG. 8. θ-2θ x-ray diffraction pattern of 150-nm films of NKN and NKT on single-crystal (100) LAO. The substrate peak is marked with an asterisk. Rocking curves (Ω scan) are shown in the inset.

TABLE II. *a* lattice constants and full-width at half maximum-(FWHM) values of the rocking curves and phi reflections for NKT, NKN, and NKTN films on LAO (uncertainty in the last digit is indicated parenthetically).

| | Lattice constant (Å) | FWHM of [100] rocking curve on $LaAlO_3$ | FWHM of [220] ϕ scan on $LaAlO_3$ | Lattice-constant mismatch with $LaAlO_3$ |
|---|---|---|---|---|
| NKT | 3.85(1) | 0.49(5)° | 0.89(5)° | 1.5% |
| NKN | 3.89(1) | 0.57(5)° | 1.28(5)° | 2.5% |

cube-on-cube epitaxy. Representative ϕ-scans and pole figures of 3-layer (1500 Å) films of NKN and NKT on LAO are shown in Fig. 9, and the FWHM of ϕ scans for NKN and NKT on LAO are reported in Table II. These measurements show that the films are not only *c*-axis aligned, but aligned in-plane as well. The narrowness of the ϕ scan peaks is also indicative of good crystallinity.

### H. Surface morphology

Figure 10 is a representative atomic force micrograph (AFM) of a 3-layer (1500 Å) NKT film on LAO and

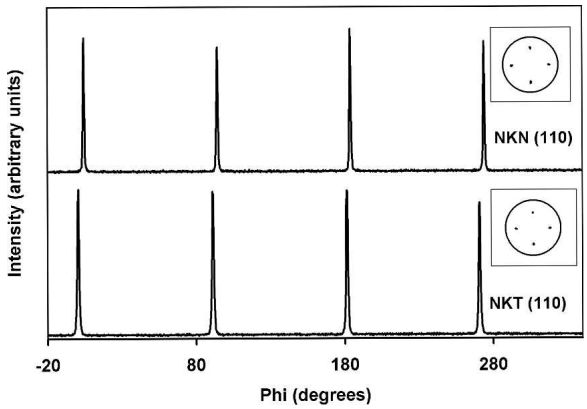


FIG. 9. ϕ scan taken about the NKN (220) reflection from a 150 nm NKN film on single crystal (100) LAO. Pole figures are shown in the inset.

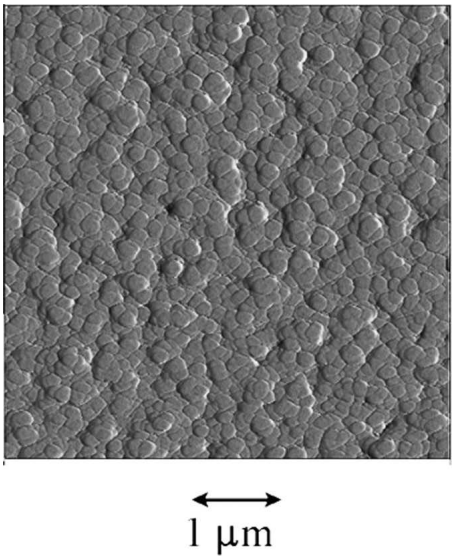


FIG. 10. Atomic force micrograph of a 150-nm film of NKT on single-crystal (100) LAO.

annealed at 700 °C. The AFM scan of this film indicated root mean square roughness of 7.5 ± 1.5 nm. As in the previous sol-gel synthesis of polycrystalline NKN films,[9] the films are fairly rough. In addition, there are some voids and cracks in the film visible through scanning electron microscopy. The cracking and voiding may be due to the rapid loss of solvent caused by the rapid heating of the sample. In previous studies, we have found that rapid heating leads to superior epitaxy, but in this case a lower temperature drying step may be helpful.

## IV. CONCLUSIONS

*c*-axis-aligned, epitaxial films of NKT and NKN were successfully grown on single-crystal LAO substrates using a non-vacuum, all alkoxide, solution route. Films were comparable in crystalline quality to those deposited by high vacuum sputtering and may provide a low-cost large area alternative to vacuum processing.

## ACKNOWLEDGMENTS

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