Epitaxial (110) orthorhombic KNbO₃ thin films were prepared using alkoxide solutions. Single-phase films were produced with stoichiometric sols while slight variations in stoichiometry (52/48 Nb/K or 48/52 Nb/K) created residual second phases. Nucleation and growth of KNbO₃ as a function of process conditions were monitored by observing the KNbO₃ rosettes produced from niobium-rich solutions. Methanolic solutions produced films with the highest KNbO₃ rosettes produced from niobium-rich solutions. Methanolic solutions also promoted the formation of second phases. Hydrolysis of the sol aided the crystallization of the KNbO₃ phase but also promoted the formation of second phases. Hydrolysis at 0°C reduced second-phase formation.

I. Introduction

KNbO₃ thin film ferroelectrics have high electrooptic coefficients and moderate dielectric constants which make them ideal for use as high-speed electrooptic devices, optical waveguides, and frequency doublers. However, device-quality thin films have proved to be difficult to synthesize. Sol-gel is a relatively simple technique that offers the advantage of a low-temperature, low-cost method to produce crystalline KNbO₃ thin films. Oriented and epitaxial KNbO₃ films have been grown on single-crystal MgO and SrTiO₃ substrates via sol-gel methods, although limited success has been achieved on optimization of these films.

KNbO₃ is cubic at the crystallization temperature (typically 700–800°C for sol-gel-derived films). The ferroelectric Curie point occurs at 435°C when it converts to the tetragonal form. Below 225°C KNbO₃ is orthorhombic. Figure 1 shows how the pseudocubic and orthorhombic crystal structures are related. The crystallographic notation used in this paper will be for the orthorhombic unit cell and not the pseudocubic unit cell, which has been used by some researchers.

Synthesis of multicomponent crystalline oxides by the sol-gel process is often complicated by precipitation and phase separation resulting from different hydrolysis rates of the individual component metallo-organic (often alkoxide) species used as precursors. Previous research has shown that the formation of a double alkoxide species prior to hydrolysis often alleviates this problem. The association of the metals through an oxygen bond unifies the rate of hydrolysis and allows for better mixing of the components. However, the lithium niobium double ethoxide has been successfully synthesized and used to form LiNbO₃ films, the analogous potassium niobium double ethoxide has lower stability.

Various schemes have been used to create a stable potassium niobium double alkoxide solution for sol-gel film deposition including forming a double ethoxide which was hydrolyzed with a methanol/water solution, preparing a solution of niobium ethoxide and potassium hydroxide in methanol, forming a double methoxyethanol solution, and modifying the double ethoxide solution with 2-ethylhexanoic acid. A comparison of these results suggests that using methanolic solutions promotes the formation of single-phase films, an unexpected result since the double methoxide should dissociate more easily than the double ethoxide.

Little work to date has focused on the influence of solution chemistry on the development of microstructure in the films. This paper presents the results of microstructural changes due to varying process parameters such as stoichiometry, precursor chemistry, water of hydrolysis, hydrolysis temperature, aging of the solution, and aging of the sol. Both stoichiometric and slightly nonstoichiometric sols were used in order to study the effect of processing conditions on nucleation and crystal growth in KNbO₃ sol-gel-derived thin films.

II. Experimental Procedure

All reactions and manipulations were carried out under dry nitrogen using standard Schlenk techniques. Methanol and ethanol were dried by distillation over molecular sieves. Benzene was dried by distillation over calcium hydride. Potassium ethoxide (KOEt) and potassium methoxide (KOME) were prepared from the metal. The potassium content was determined by hydrolysis followed by titration of KOH against 0.1N HCl. Niobium ethoxide [Nb(OEt)₅] (Alfa Products, Danvers, MA) was distilled (142°C, 0.1 mmHg) prior to use. The distilled niobium ethoxide was diluted with ethanol to form a 1M stock solution.

![Fig. 1. Relationship between pseudocubic and orthorhombic KNbO₃ unit cells.](image-url)
Three multicomponent solutions were prepared to investigate the effect of the precursor chemistry on the resulting films. First, K(OEt) and Nb(OEt), were combined in ethanol to form a solution which was 0.9M in K. This solution was refluxed for 24 h to promote the formation of the double ethoxide, KNb(OEt),. The solution was diluted with ethanol to form a solution which was 0.26M in K. This solution will be referred to as the “ethoxide solution.” For the second solution, K(OEt) and Nb(OEt), were combined in ethanol. Ethanol was removed by evaporation, resulting in crystallization of the double ethoxide. This solid was dissolved in methanol to form a solution which was 0.26M in K. This will be referred to as the “methoxide solution.” It is expected that there was either partial or complete alcohol exchange in the solution. Three stoichiometric ratios of Nb/K were used in the methoxide solutions, niobium-rich (52% niobium, 48% potassium), potassium-rich (52% potassium, 48% niobium), and equimolar (50% niobium, 50% potassium). For the third solution, Nb(OEt), and anhydrous potassium acetate (KC,H,O,) (Aldrich Chemical Co., Milwaukee, WI) were mixed in ethanol and refluxed for 24 h. The resulting solution was 0.20M in K. This will be referred to as the “acetate solution.” All solutions were analyzed for K and Nb concentrations by flame atomic absorption. The solutions were hydrolyzed by the addition of a 2.5M solution of deionized water in methanol in a ratio of 0.2 mol of water per mole of alkoxide (designated 0.2/1). Hydrolysis was performed on sols which were either at room temperature or cooled in an ice bath. A control methoxide sol was prepared without hydrolysis.

Single-crystal (100) MgO substrates (Commercial Crystal Labs, Naples, FL; Harrick Scientific Corp., Ossining, NY) were ultrasonically cleaned in acetone followed by vapor degreasing with trichloroethylene immediately prior to spin coating. Spin-coated films were prepared by placing a few drops of the sol onto the substrates followed by spinning at 3000 rpm for 30 s in air. The coated substrates were immediately inserted into a hot tube furnace and held for 1 h at 320°C under flowing oxygen. These steps were repeated three times to achieve the desired thickness of approximately 2000 Å. The films were crystallized by insertion into a hot tube furnace and held for 4 h at 800°C under flowing oxygen.

The X-ray spectra of the films were measured using the powder diffraction method (Model D5000 diffractometer, Siemens, Germany; Model APD 3720 vertical powder diffractometer, Philips Electronics Instruments, Netherlands). The amount of (110) preferred orientation in the films was calculated based on the intensity ratio between the (111) and (110) diffraction peaks in polycrystalline KNbO, (JCPDS 32-822). Scanning electron microscopy (SEM) (JSM-840 JEOL, Japan) was performed in both the backscattered and secondary electron modes. Also, an energy dispersive X-ray spectrometer (EDS) (9900 EDAX, Mahwah, NJ) was used for X-ray mapping of the films. Microstructural features were studied with an analytical transmission electron microscope (TEM) (CM20, Philips) at 200 keV equipped with an EDS (9800, EDAX). TEM samples were prepared using standard dimpling and ion milling techniques, as well as a chemical etch technique. A Raman spectrometer (Ramanor U-1000, Instruments S.A., Edison, NJ) coupled to a research-grade microscope, was used to confirm phase identification in the films.

III. Results

1) Variations in Stoichiometry

Three different stoichiometric ratios of potassium to niobium (52/48, 50/50, and 48/52) in the methoxide solution were studied. These solutions were hydrolyzed with 0.2 mol of water per mole of alkoxide at 0°C and spun 1 h after hydrolysis. Subsequent heat treatment involved 4 h at 800°C. X-ray powder diffraction shows that all of the KNbO, films grew with strong (110) orientation (Fig. 2). The major X-ray diffraction peak of these films at 4.038 Å is closer to the orthorhombic (110) spacing of 4.035 Å than the orthorhombic (001) spacing of 3.987 Å. The amount of preferred (110) orientation in the films is 90% for the equimolar, 85% for the potassium-rich, and 98% for the niobium-rich film. The films derived from the equimolar solution were single-phase while the slightly non-stoichiometric solutions produced films with second phases.

The microstructure of the film changed significantly depending on the stoichiometry of the sol, evident in the optical micrographs of the films (Fig. 3). Potassium-rich films exhibit appreciable optical scatter due to cracking and grain boundary phases (Fig. 3(A)). Equimolar films had a uniformly smooth microstructure (Fig. 3(B)). Niobium-rich films contain rosettes in a darker matrix (Fig. 3(C)).

The single-phase films derived from the equimolar solutions were (110) oriented and epitaxial with respect to the (100) MgO substrate (Fig. 4). The orientation of the film to the substrate was (110) KN || (100) MgO and [001] KN || [001] MgO according to the TEM diffraction patterns. Although optical microscopy showed a fairly uniform contrast, the TEM micrographs showed low-angle grain boundaries with a misorientation of approximately 1° between grains, indicating a small amount of in-plane misorientation. The grains also contained 50-nm pores which were faceted along [110] and [001]. Ferroelectric domains can be seen in some of the grains (Fig. 4(B)).

When niobium-rich sols were used, full crystallization of the film to KNbO, after heat treatment did not occur. SEM X-ray maps of potassium and niobium in these films revealed that the matrix contained little potassium while niobium was spread...
evenly throughout the film (Fig. 5). Raman microprobe spectra of the rosettes confirmed that they are orthorhombic KNbO$_3$ while the matrix exhibited no appreciable Raman scatter (Fig. 6). TEM analysis showed that the rosettes are single-crystal epitaxial KNbO$_3$ with the same orientation relationship as in the equimolar films (Fig. 7(A)). The electron diffraction pattern results from double diffraction between the potassium niobate film and the MgO substrate. The matrix is made up of mostly niobium-rich (determined by EDS) needlelike crystals with random orientations (Fig. 7(B)) and some flat platelets. Characteristic $d$-spacings in the Nb-rich region are 8.04, 3.90, 3.77, 2.84, 2.53, 2.30, and 1.95 Å. These $d$-spacings (except 8.04 Å) and the niobium/potassium ratio agree with K$_2$Nb$_2$O$_7$ (JCPDS 31-106), K$_3$Nb$_2$O$_7$ (JCPDS 21-1095) has all but the 3.90-Å $d$-spacing. The loss of potassium will be discussed in a future paper.

Higher magnification of the rosettes shows ferroelectric domains present in the rosettes with domain wall orientation along [110] planes (Fig. 8). Interestingly enough, the rosettes were not microporous, only containing micrometer-size voids.
where the rosette arms grew together. Moire fringes in Fig. 8(B) indicate a rotational misorientation of \(<1^\circ\) between (220)_{film} and (200)_{substrate}.

Each rosette in the niobium-rich films represents a nucleation site in the film. This provided us with an easy technique using optical microscopy to monitor changes in nucleation density and amount of KNbO₃ produced with various processing conditions by using niobium-rich films.

(2) Systematic Precursor Modifications

Niobium-rich thin films were prepared using ethoxide, methoxide, and acetate sols (Figs. 9(A–C)). Hydrolysis of the ethoxide solution resulted in the formation of a white precipitate which cleared after stirring for 1 day. The acetate and methoxide solutions hydrolyzed without precipitation. The methoxide solution produced films with the highest nucleation density and the most KNbO₃. The films were smooth with low optical scatter (Fig. 9(A)). Films prepared from the ethoxide and acetate solutions produced crystalline KNbO₃ grains but exhibited significant scatter due to the presence of second phases and porosity/voids (Figs. 9(B) and (C)). As these initial results showed that the methoxide solution produced the highest-quality films, the subsequent processing effects were studied using only the methoxide solution.

(3) Variations in Hydrolysis

The water of hydrolysis added to the solutions was critical for the development of the microstructures discussed above (Figs. 10(A–D)). Spinning of unhydrolyzed niobium-rich methoxide sols resulted in films with little KNbO₃ crystallization (Fig. 10(A)). These films showed 6% coverage with KNbO₃ rosettes with an average size of 125 \(\mu\)m. Water vapor added
Fig. 7. TEM micrographs of rosette and matrix: (A) epitaxial orthorhombic KNbO₃ rosette and (B) needlelike niobium-rich second phase.

Fig. 8. (A) 90° ferroelectric domains in KNbO₃ rosette in niobium-rich film with domain boundary orientations along {111}. (B) Moire fringes indicating <1° misorientation between the film and the substrate.

during the drying of the film by bubbling O₂ through water at 23°C increased crystallization in the films, with coverage of 24% and with a rosette size of 175 μm (Fig. 10(B)). These films with a low concentration of KNbO₃ showed the formation of a dark phase on the surface after 1-week exposure to air, suggesting inherent instability of the matrix phase. However, a new crystalline phase was not detected by XRD. Hydrolysis with 0.2 mol of water per mole of alkoxide prior to spinning resulted in an increase in rosette coverage to 52% with 6-μm rosettes when the solution was at room temperature during hydrolysis (Fig. 10(C)). Hydrolysis at 0°C (rather than room temperature) increased the amount of KNbO₃ further to 81% with 5-μm rosettes (Fig. 10(D)).

(4) Aging
Films of the niobium-rich solutions, which were spin coated later than 1 h after hydrolysis, had increased amounts of second phases and fewer KNbO₃ rosettes (Figs. 11(A–D)). The microstructure of the films also changed with increasing storage time between the preparation of the methoxide solution and the addition of water/methanol solution for hydrolysis (Figs. 12(A–D)). Niobium-rich solutions, which were aged for 1 month prior to hydrolysis, resulted in films with increased amounts of second phases and less KNbO₃ compared to unaged solutions (Figs. 12(A) and (B)). After storage for longer than 1 month prior to hydrolysis, immediate precipitation resulted upon the addition of water. Unaged equimolar solutions produced single-phase orthorhombic KNbO₃ films with a (110) preferred orientation, but aging between preparation and hydrolysis resulted in films with KNbO₃ rosette formation similar to that observed for the niobium-rich compositions (Figs. 12(C) and (D)).

IV. Discussion
Single-phase epitaxial KNbO₃ thin films can be formed on (100) MgO substrates by the sol-gel technique using methanolic solutions under certain conditions. A summary of the process
results is shown in Table I. First, an equimolar ratio of potassium and niobium in the solution is necessary to avoid the formation of second phases. This is not surprising considering that K\textsubscript{2}NbO\textsubscript{5} is a line compound. Hydrolysis of this equimolar solution at 0°C prior to spinning enhances the formation of orthorhombic K\textsubscript{2}NbO\textsubscript{5} provided that the films are prepared immediately after the hydrolysis step. Furthermore, the methanolic solution produces single-phase films only if the hydrolysis step is performed promptly after the potassium niobium double ethoxide is dissolved in methanol.

Crystallization during the 750–800°C heat treatment occurs at a temperature where the cubic structure would be stable. The film should convert first to the tetragonal form and then to the orthorhombic form upon cooling. Distinguishing between the cubic, tetragonal, and orthorhombic phases in oriented thin films by standard X-ray techniques through the observation of peak splitting is difficult. However, Raman microprobe analysis confirmed that orthorhombic K\textsubscript{2}NbO\textsubscript{5} is formed in these thin films, despite any residual stresses resulting from thermal expansion coefficient mismatch, lattice mismatch with the substrate, or volume change upon crystallization (Fig. 6).

The nature of the nucleation and growth of these mixed phase films can explain the changes in microstructure which were observed. Films derived from both equimolar and niobium-rich solutions crystallize by formation of K\textsubscript{2}NbO\textsubscript{5} nuclei which grow laterally throughout the film until the potassium component of the film is consumed. Growth of K\textsubscript{2}NbO\textsubscript{5} grains in niobium-rich films is arrested at the stage where insufficient potassium remains in the matrix to form K\textsubscript{2}NbO\textsubscript{5} (Fig. 5). However, for the equimolar solutions, crystallization leads to single-phase films in which the K\textsubscript{2}NbO\textsubscript{5} crystals have coalesced. This process occurs rapidly at 800°C and low-angle grain boundaries are formed upon coalescence. The 5% lattice mismatch with MgO would contribute to the formation of low-angle grain boundaries, which have also been observed in ion-beam-sputtered K\textsubscript{2}NbO\textsubscript{5} films on MgO.\textsuperscript{4}

Porosity has been a problem in other K\textsubscript{2}NbO\textsubscript{5} sol-gel films.\textsuperscript{16} However, the rosettes in the niobium-rich films are dense, except where the dendritic arms grew together (Figs. 7 and 8). Films derived from the niobium-rich solutions should crystallize more slowly because the growth rate should be dependent on diffusion of potassium and niobium. However, as the amount of potassium in the films increases to an equimolar ratio, long-distance diffusion is not necessary. Crystallization could occur more quickly, trapping pores in the grains. These pores facet along low-energy/high-density {110} and {001} planes. The absence of fast diffusion paths such as grain boundaries near the pores would prevent the removal of intergranular porosity.\textsuperscript{17} We speculate that slowing the growth rate of the K\textsubscript{2}NbO\textsubscript{5} grains would decrease the porosity in the films, by allowing for densification prior to complete crystallization.

### Table I. Process Parameters and Their Effects on K\textsubscript{2}NbO\textsubscript{5} Thin Film Microstructure

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>Microstructural change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decreasing potassium content (substoichiometric)</td>
<td>Lower rosette concentration, lower porosity</td>
</tr>
<tr>
<td>Methanolic rather than ethanolic solutions</td>
<td>Higher rosette concentration, lower porosity</td>
</tr>
<tr>
<td>Increasing amount of water</td>
<td>Higher rosette concentration</td>
</tr>
<tr>
<td>Lowering temperature of hydrolysis</td>
<td>Higher rosette concentration</td>
</tr>
<tr>
<td>Solution aging before hydrolysis</td>
<td>Lower rosette concentration</td>
</tr>
<tr>
<td>Solution aging after hydrolysis</td>
<td>Lower rosette concentration</td>
</tr>
</tbody>
</table>

Fig. 9. Optical micrographs for (A) methoxide, (B) ethoxide, and (C) acetate derived films.
The density of the KNbO₃ films affects the formation of ferroelectric domains. Whereas pore-free regions of niobium-rich films had clearly defined ferroelectric domains (Fig. 7), the high amount of porosity in the equimolar films resulted in few grains with clear ferroelectric domain structures (Fig. 4). The high surface area and distortion of the crystal structure at the surface and the accommodation of strain energy at the pore surfaces would minimize the formation of ferroelectric domains.¹⁸

Each rosette observed in the optical and electron micrographs represents an individual nucleation site. The evaluation of the nucleation density in films prepared under various processing conditions allows us to monitor the effects of each condition on crystallization of KNbO₃ films. These observations were especially valuable in the interpretation of hydrolysis and aging behavior.

When slightly niobium-rich methoxide solutions were hydrolyzed at reduced temperatures immediately prior to spinning, films with small amounts of second phases were produced (Fig. 10(D)). When hydrolysis was done at room temperature or the hydrolyzed sol was allowed to age, the number of KNbO₃ rosettes formed in the films decreased (Figs. 10(C) and 11). The total amount of orthorhombic KNbO₃ phase in the films was reduced; the amount of second-phase growth greatly increased. These results indicated that the nucleation of KNbO₃ rosettes in the crystallizing films depends upon a homogeneous distribution of potassium and niobium in the hydrolyzed sol. Initially, when the double ethoxide is dissolved in methanol, the solution consists of the double ethoxide in a solvent of methanol. The double ethoxide is more stable (lower tendency to dissociate into its parent alkoxides) than the double methoxide,¹²,¹³ but methanolic solutions show a lower tendency to precipitate in the presence of water.⁵,⁶ Alcohol exchange in alkoxide solutions generally occurs quickly and can exchange either completely or partially depending on the alkoxide system, but the exchange reaction is promoted toward the alcohol in greater abundance.¹³ Therefore, it is expected that the vast majority of the ethoxy groups will quickly undergo alcohol exchange with the solvent, resulting in a partial or complete conversion of the double ethoxide to the methoxide. It is also well known that niobium alkoxide monomers coordinate with each other both in the pure compound and in solution.¹⁷ Increasing the temperature of the solution increases the conversion to the double methoxide and increases the rate of hydrolysis. Both of these processes are likely to lead to a reduced association between potassium and niobium in the solution through the decomposition of the double alkoxide, and the formation of extended niobium oxo-alkoxide species in the solution. Similarly, when the sol which is hydrolyzed at reduced temperature
is allowed to age (at room temperature) for 1 or more days (Fig. 11), the distribution of potassium and niobium in the sol may be disturbed by reactions such as those discussed above: conversion of the double ethoxide to the less stable double methoxide, and growth of extended niobium-containing clusters through various condensation and redistribution reactions.

The deterioration of film quality which is observed when unhydrolyzed methoxide solutions are aged between their preparation and the time of hydrolysis supports this model. As the solution is stored, more of the double ethoxide will be converted to the double methoxide. Films spun from these aged solutions should then be less homogeneous than the unaged solutions, causing the resulting films to have fewer nucleation sites and less KNbO₃ in the films, as was observed (Fig. 12).

Hydrolysis of the solution, as well as adding water vapor during the drying process, resulted in increased crystallization in the films compared to the unhydrolyzed samples (Fig. 10). It has been shown that the water of hydrolysis plays a key role in the crystallization of LiNbO₃ alkoxide gels which possess an atomic arrangement near that of crystalline LiNbO₃. It is speculated that the addition of water to the potassium niobium alkoxide solutions may also result in the formation of clusters which act as nucleating sites for KNbO₃. Further studies in process confirm that increasing amounts of water of hydrolysis aid the nucleation of KNbO₃.

V. Conclusions

Single-phase epitaxial (110) oriented thin films of KNbO₃ can be made on (100) MgO substrates by the sol-gel technique. Methoxide solutions produce films in which KNbO₃ crystallizes more easily than ethoxide or acetate solutions. The double methoxide is unstable and must be used soon after alcohol exchange from the double ethoxide to avoid the formation of a second phase. Prehydrolysis and hydrolysis at lower temperatures aid in the crystallization of the KNbO₃ phase. Small deviations from stoichiometry (±2%) generate significant amounts of second phase and changes in the microstructure in the films. Only films with exact equimolar Nb/K ratios were single phase. Niobium-rich films formed K₂Nb₅O₁₀ and K₂Nb₂O₇ in addition to KNbO₃. Porosity increased with the amount of potassium in the films and is linked to rapid crystallization. The highest-density KNbO₃ grains were formed from niobium-rich sols where the crystallization rate was slowed by requiring long-distance diffusion of potassium and niobium.
Fig. 12. KNbO₃ rosette concentration variations due to aging of solution prior to hydrolysis: (A) unaged 50/50 Nb/K, (B) aged 50/50 Nb/K, (C) unaged 50/50 Nb/K, and (D) aged 50/50 Nb/K.

References


12. B. Tuttle; private communication.


