journal

J. Am. Ceram. Soc., 74 [1] 53–59 (1991)

Synthesis of Potassium Niobate from Metal Alkoxides

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Preparation of potassium niobate from metal alkoxides was investigated. Potassium-niobium ethoxide, $KNb(OC_2H_5)_6$, and potassium-niobium propoxide, $KNb(OC_3H_7)_6$, were synthesized and subsequently hydrolyzed using several water concentrations (0.75 to 6.0 mol of water/(mol of alkoxide)). Rapid precipitation of potassium-deficient particles occurred when higher concentrations of water were used. This resulted in the formation of a multiphase material after calcination, as X-ray diffraction showed the presence of both $KNbO_3$ and potassium-deficient oxide phases(s). Single-phase $KNbO_3$ could be prepared by two methods: (1) hydrolysis of $KNb(OC_3H_7)_6$/propanol solutions using 1 mol of water (per mole of propoxide) added as a water/propanol solution and (2) hydrolysis of $KNb(OC_2H_5)_6$/ethanol solutions using 1 mol of water (per mole of ethoxide) added as a water/methanol solution. The latter method provided advantages of low calcination temperature for the formation of single-phase $KNbO_3$ and low weight loss after calcination. [Key words: niobates, synthesis, alkoxide, hydrolysis, potassium.]

I. Introduction

POTASSIUM NIOBATE ($KNbO_3$), a ferroelectric material with high electrooptic and nonlinear optical coefficients and good photorefractive properties, is of interest for applications in optical waveguides, frequency doublers, and holographic storage systems.[1-3] Potassium niobate powders and single crystals are generally prepared using potassium carbonate and niobium oxide as the starting materials.[4-7] However, because of the relatively coarse scale of mixing of the reactants, it is often difficult to achieve a homogeneous, single-phase product. In recent years, there has been considerable emphasis on fabrication of multicomponent ceramics, glasses, and composites using chemical processing routes which result in more intimate mixing (e.g., molecular-scale or nanometer-scale) of the components. Many investigations have been reported concerning "sol-gel" processing of ferroelectric materials, including barium titanate, lead zirconate titanate, and lithium niobate.[8-20] However, relatively few studies of sol–gel processing of potassium niobate have been carried out. Wu *et al.*[21] reported the synthesis of potassium niobate from potassium and niobium ethoxide precursors. However, those authors noted that single-phase $KNbO_3$ could not be formed, as precipitates were always deficient in potassium. Swartz *et al.*[22] used potassium and niobium methoxyethoxides to prepare potassium niobate. A mixed alkoxide solution was hydrolyzed, dried, and subsequently calcined at 800°C. The product was reported to be single-phase $KNbO_3$, although X-ray diffraction (XRD) data were not presented. In contrast to the bulk sample, thin films prepared in a similar manner had unidentified second phase(s) according to XRD results.[22] Tuttle and co-workers[23] recently synthesized single-phase $KNbO_3$ powders and thin films using niobium ethoxide and potassium hydroxide as reactants. As in the study by Swartz *et al.*, differences in phase development during heat treatment were observed for bulk gels vs thin films. In some thin-film samples, a potassium-deficient phase, $K_4Nb_6O_{17}$, and a "low-temperature," non-perovskite $KNbO_3$ phase were observed. These phases could be eliminated by careful control over the calcination procedure.

The present investigation was undertaken to identify processing conditions for low-temperature synthesis of single-phase perovskite $KNbO_3$ from alkoxides. Ethoxides and propoxides of potassium and niobium were used as the precursor materials. In this paper, we report on the synthesis and characterization of the alkoxides and the resulting oxides produced after the processing steps of hydrolysis/condensation, drying, and calcination.

II. Experimental Procedure

(1) Synthesis

All reactions and manipulations were carried out under dry nitrogen using standard Schlenk techniques.[24] Ethanol was dried and distilled over sodium, benzene was dried over sodium and benzophene, and 1-propanol was used as received.

Niobium ethoxide, $Nb(OC_2H_5)_5$, was prepared using the procedure of Bradley *et al.*[25] In a typical reaction, 25 g of niobium chloride, $NbCl_5$,* was initially mixed with 750 mL of benzene. Then 100 mL of ethanol was added under vigorous stirring to form $Nb(OC_2H_5)_5$ according to

$$NbCl_5 + 5C_2H_5OH = Nb(OC_2H_5)_5 + 5HCl \qquad (1)$$

Ammonia was then bubbled through the reaction vessel in order to convert the side product, HCl, to ammonium chloride. The ammonium chloride precipitate was subsequently removed by filtration and the filtrate was distilled under ambient pressure in order to remove benzene and excess ethanol. The resulting product was a viscous liquid which was vacuum distilled to produce high-purity niobium ethoxide (boiling point 145°C at 0.1 mmHg).

Potassium ethoxide, KOC_2H_5, was prepared from potassium† and ethanol. In a typical procedure, 3.9 g (0.1 mol) of potassium was reacted with 4.6 g (5.8 mL) of ethanol. A solid product was obtained, which was dissolved in ethanol to prepare a 1.0*M* stock solution.

A bimetallic, or "double," ethoxide was prepared by reacting the potassium and niobium ethoxides. In a typical procedure, 10 g (0.031 mol) of niobium ethoxide was dissolved in 20 mL of ethanol and subsequently mixed with 31 mL of the 1.0*M* potassium ethoxide stock solution. After refluxing for 24 h, the solution was diluted with ethanol to prepare a

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L. C. Klein—contributing editor

Manuscript No. 197651. Received April 10, 1990; approved August 27, 1990.

Supported by the National Science Foundation, Division of Materials Research, Ceramics and Electronic Materials Program (DMR-8451916) and the Defense Advanced Research Projects Agency (MDA972-88-J-1006).

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†Fisher Scientific, Pittsburgh, PA.

0.25*M* stock solution. In order to prepare samples for spectroscopic and elemental analysis, a concentrated potassium-niobium ethoxide solution was first crystallized at −20°C.[‡] Solvent (i.e., ethanol) was then withdrawn, using a syringe. Residual solvent was subsequently removed by pulling a vacuum, and solid white powder remained.

Potassium propoxide, niobium propoxide, and potassium-niobium propoxide were prepared using procedures similar to those described above except that 1-propanol was used as a reactant instead of ethanol.

Alkoxides were hydrolyzed using water concentrations in the range 0.75 to 6.0 mol of water/(mol of alkoxide). Potassium-niobium ethoxide/ethanol solutions were hydrolyzed by adding either water/ethanol or water/methanol solutions, while potassium-niobium propoxide/propanol solutions were hydrolyzed using water/propanol solutions. Reactions were allowed to continue for approximately 1 d after the water addition. Solvents were removed either by filtration or by evaporation, followed by drying in air (~60° to 80°C) for approximately 1 d. After drying, powders were calcined in air for 5 h at temperatures in the range 150° to 850°C.

(2) Characterization

Ethoxides were characterized by nuclear magnetic spectroscopy (NMR)[§] and mass spectroscopy.[¶] Proton NMR spectra were obtained for niobium ethoxide dissolved in deuterated toluene ($C_6D_5CD_3$), potassium ethoxide dissolved in a deuterated dimethyl sulfoxide (CD_3SOCD_3), and niobium-potassium ethoxide dissolved in deuterated benzene (C_6D_6). Mass spectra (MS) for niobium ethoxide liquid and potassium-niobium ethoxide powder were obtained using an accelerating voltage of 70 eV. Elemental analyses for carbon and hydrogen were carried out for the potassium-niobium ethoxide.[**]

Dried products obtained after hydrolysis/condensation reactions were characterized by thermal gravimetric analysis (TGA)[††] and differential thermal analysis (DTA).[††] Analyses were carried out in air at a heating rate of 5°C/min. Phases in calcined samples were determined using X-ray diffraction (XRD).[‡‡] Elemental analysis for niobium and potassium was carried out on selected samples.[**]

III. Results and Discussion

(1) Characterization of Ethoxides

Proton NMR data for the potassium, niobium, and potassium-niobium ethoxides are shown in Table I. Potassium ethoxide showed a quartet (δ = 3.45 to 3.53 ppm) which originated in the α-proton (CH_2) resonances and a triplet (δ = 0.90 to 0.96 ppm) which originated in the β-proton (CH_3) resonances. Niobium ethoxide showed two triplets (δ = 1.25 to 1.30 and 1.37 to 1.42 ppm) and two quartets (δ = 4.35 to 4.40 and 4.48 to 4.55 ppm). Two triplets and quartets are observed because of the dimeric nature of niobium ethoxide.[27] (CH_2 and CH_3 protons are associated with both bridging and terminal alkoxy groups in the dimeric molecule.) The "mixed-metal" alkoxide shows a triplet (δ = 1.36 to 1.40) and a quartet (δ = 4.44 to 4.51). The absence of CH_2 protons at δ = 3.45 to 3.53 indicates coordination of potassium ethoxide to niobium ethoxide, providing clear evidence for the formation of a bimetallic potassium-niobium alkoxide.

Table I. Proton NMR Data

Compound	Solvent	CH_2(q)*	CH_3(t)*
$K(OC_2H_5)$	$(CD_3)_2SO$	3.45–3.53	0.90–0.96
$Nb(OC_2H_5)_5$	$C_6D_5CD_3$	4.35–4.40 4.48–4.55	1.25–1.30 1.37–1.42
$KNb(OC_2H_5)_6$	C_6D_6	4.44–4.51	1.36–1.40

*q = quartet, t = triplet.

Mass spectra (MS) for niobium ethoxide and potassium-niobium ethoxide are shown in Table II. The presence of the $Nb(OC_2H_5)_7H^+$ fragment is consistent with the dimeric character of niobium ethoxide. The presence of the $KNb(OC_2H_5)_5^+$ fragment provides further evidence for the formation of the bimetallic alkoxide.

Analysis of the potassium-niobium ethoxide powder showed 35.3 wt% carbon and 7.2 wt% hydrogen. These values are in good agreement with the calculated values of 35.82 wt% carbon and 7.51 wt% hydrogen for $KNb(OC_2H_5)_6$.

(2) Effects of Processing Conditions on Phase Development and Chemical Composition

Qualitative observations made during the initial experiments indicated that the molar ratio of water/alkoxide had a significant effect on the hydrolysis/condensation reaction kinetics and on the product physical and chemical characteristics. In one experiment, a clear solution of 0.25*M* potassium-niobium ethoxide in ethanol was divided into three portions to which different amounts of water were added (5.0, 2.5, and 0.75 mol of water/(mol of ethoxide)). Water was added as a 2.5*M* solution in ethanol. The solution containing 5.0 mol of water/(mol of ethoxide) became opaque immediately, and rapid sedimentation of precipitated particles was evident within a few minutes. As the amount of water added to the ethoxide solution was decreased, the time required for solutions to become cloudy and for particle sedimentation to occur increased. For example, the solution hydrolyzed with 0.75 mol of water/(mol of ethoxide) remained clear for several hours before any precipitation became evident.

The precipitated particles obtained in the above experiment were collected by filtration, dried at ~80°C, and calcined at various temperatures. Figure 1 shows the results of XRD analysis on samples which were prepared with 5 mol of water/(mol of ethoxide). Uncalcined powder and powder calcined at 475°C were both amorphous. Weak crystallization was observed after calcination at 600°C, but most of the peaks were *not* associated with $KNbO_3$. The major crystalline phase(s) appeared to be a mixture of "potassium-deficient" compounds, i.e., $K_2Nb_3O_8$, $K_4Nb_6O_{17}$, and $K_4Nb_6O_{17}\cdot 3H_2O$.[§§,28] Identification was uncertain, however, because some of the expected peaks were not observed and peak intensities were not always consistent with the JCPDS references. With increasing calcination temperature, crystallization of $KNbO_3$ became more extensive, while the peak intensities for the potassium-deficient phases showed little change. The latter observation suggested that the development of potassium-deficient phases could not be attributed to preferential volatilization of K_2O from $KNbO_3$. Instead, the results indicate that the precipitated particles were potassium deficient. This was confirmed by chemical analysis which showed that powder dried at 150°C had 50.3 wt% Nb and 16.3 wt% K. This corresponds to an Nb/K mole ratio of 1.30. Powder calcined at 750°C had 58.3 wt% Nb and 19.5 wt% K, which corresponds to an Nb/K mole ratio of 1.26. The increase in the weight percentages of Nb and K upon calcination to 750°C reflect the elimination of residual solvent, hydroxyl groups, and carbonaceous material from the precipitates. (See discussion below concerning TGA and DTA results.) The fact that the Nb/K mole ratio remains essentially constant during heat treatment between 150° and 750°C indicates that the precipitates do not contain a volatile potassium-rich compound (e.g., K_2O). The high Nb/K mole

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[‡] In contrast to this investigation, Mehrotra *et al.*[26] reported that $KNb(OC_2H_5)_6$ could not be crystallized from an ethanol solution.

[§] Model VXR-300, Varian, Sunnyvale, CA.

[¶] Model MS-30, AEI Scientific Apparatus, Manchester, England.

[**] Galbraith Laboratories, Knoxville, TN.

[††] Model STA-409, Netzsch, Exton, PA.

[‡‡] Model APD 3720, Philips Electronic Instruments, Mt. Vernon, NY.

[§§] The hydrate phase probably develops from $K_4Nb_6O_{17}$ upon exposure of the powder samples to atmospheric moisture.[29]

Table II. Mass Spectra Data*

Niobium ethoxide			Potassium-niobium ethoxide		
m/e	Relative abundance	Fragment	*m/e*	Relative abundance	Fragment
409	0.1	$Nb(OC_2H_5)_7H^+$	357	5.6	$KNb(OC_2H_5)_5^+$
335	19.7	$Nb(OC_2H_5)_5OH^+$	273	100	$Nb(OC_2H_5)_4^+$
307	100	$Nb(OC_2H_5)_4(OH)_2^+$	245	12.7	$Nb(OC_2H_5)_3OH^+$
251	8	$Nb(OC_2H_5)_2(OH)_4^+$	228	11.2	$Nb(OC_2H_5)_3^+$
223	7.7	$Nb(OC_2H_5)(OH)_5^+$	217	14.7	$Nb(OC_2H_5)_2(OH)_2^+$
195	43	$Nb(OH)_6^+$	199	12.3	$ONb(OC_2H_5)_2^+$
177	71.6	$ONb(OH)_4^+$	189	18.9	$Nb(OC_2H_5)(OH)_3^+$
149	23.9	$Nb(C_2H_4)_2^+$	161	38.6	$Nb(OH)_4^+$
			143	26.6	$ONb(OH)_2^+$
			125	13.9	NbO_2^+
			45	19.1	OEt^+
			39	63.3	K^+

*Atomic mass units are based on ^1H, ^{12}C, ^{16}O, ^{39}K and ^{93}Nb.

ratio of the precipitates (i.e., relative to the double alkoxide) indicates that excess potassium remained in solution during the hydrolysis/condensation process. This was confirmed by analyzing the filtrate collected from a precipitated suspension in which the alkoxide was hydrolyzed by using 6 mol of water/(mol of ethoxide). The residual potassium concentration in solution was 0.11 wt%, while the niobium concentration was <0.0002 wt%. Although the NMR and MS data show that the potassium-niobium alkoxide was successfully synthesized, it is evident that molecular-scale mixing is disrupted at some point during subsequent processing. At this point, it is not known if dissociation of the bimetallic alkoxide occurs upon dilution (i.e., upon addition of ethanol during preparation of stock solutions) or during hydrolysis.

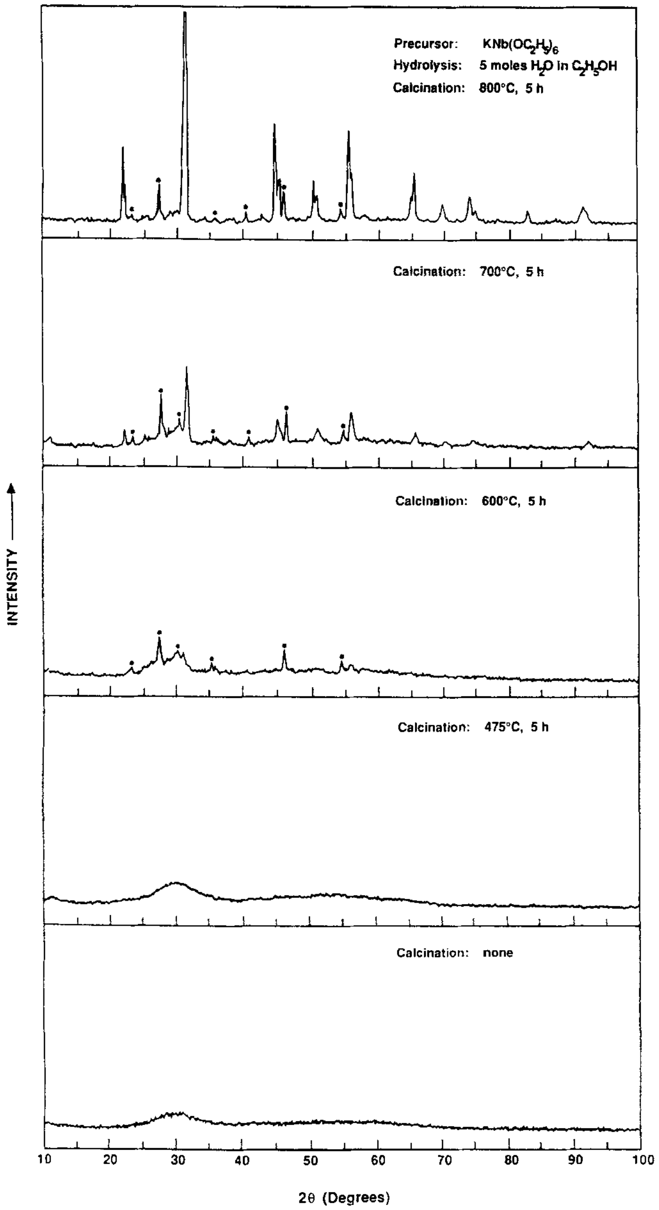

Fig. 1. XRD patterns for samples prepared with 5 mol of water per mole of potassium-niobium ethoxide which were calcined at the indicated temperature. Asterisks indicate that peaks are associated with potassium-deficient phase(s). Other peaks are for $KNbO_3$.

Figure 2 shows TGA and DTA data for a powder sample prepared using 2.5 mol of water/(mol of ethoxide). The results are very similar to those reported by Tuttle *et al.*[23] The TGA curve (Fig. 2(A)) shows that much of the weight loss (~10%) occurs upon heating to ~230°C. The DTA curve (Fig. 2(B)) shows a broad endotherm in the same temperature range, suggesting that the weight loss is due primarily to the elimination of residual solvent (ethanol), physically adsorbed water, and possibly chemically bound water (i.e., dehydroxylation). At higher temperature, a strong, broad exotherm is observed which peaks at ~525°C and has shoulders at ~430° and ~475°C. The TGA curve shows a corresponding weight loss in the same temperature range, and it is likely that these peaks are primarily associated with combustion of carbonaceous material that is present due to incomplete hydrolysis of the alkoxide. This interpretation is consistent with the observation that powders removed from the furnace in this temperature range have a black or brown color characteristic of powders with carbon chars. (The precipitated material has a white color, and powder heat-treated above ~550°C is also white.) The highest temperature portion of the strong exotherm may also be associated with the onset of crystallization. Using hot-stage XRD, Tuttle *et al.*[23] have observed crystallization of a "low-temperature," non-perovskite potassium niobate phase at temperatures as low as 500°C. However, this phase was not observed in the present study.

Figure 2(B) also shows exotherms at ~600°, ~655°, and ~750°C. The small peak at ~600°C may be associated with the crystallization of the potassium-deficient phases discussed in regard to Fig. 1. The larger peak at ~655°C is probably due to crystallization of the perovskite phase, $KNbO_3$. The small peak at ~750°C is apparently associated with further structural modification of the perovskite phase.[¶] Under

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[¶] Reisman and Holtzberg[4] reported an unexplained "heat effect" at ~730°C during a DTA study of the K_2CO_3-Nb_2O_5 phase diagram. Tuttle *et al.*[23] also observed a small exotherm at ~730°C. Using high-temperature XRD, they observed that some "low-temperature," non-perovskite potassium niobate phase remained in samples heated to 650°C (i.e., below the exotherm temperature), while only single-phase cubic $KNbO_3$ was obtained upon heat treatment to 800°C (i.e., above the exotherm temperature).

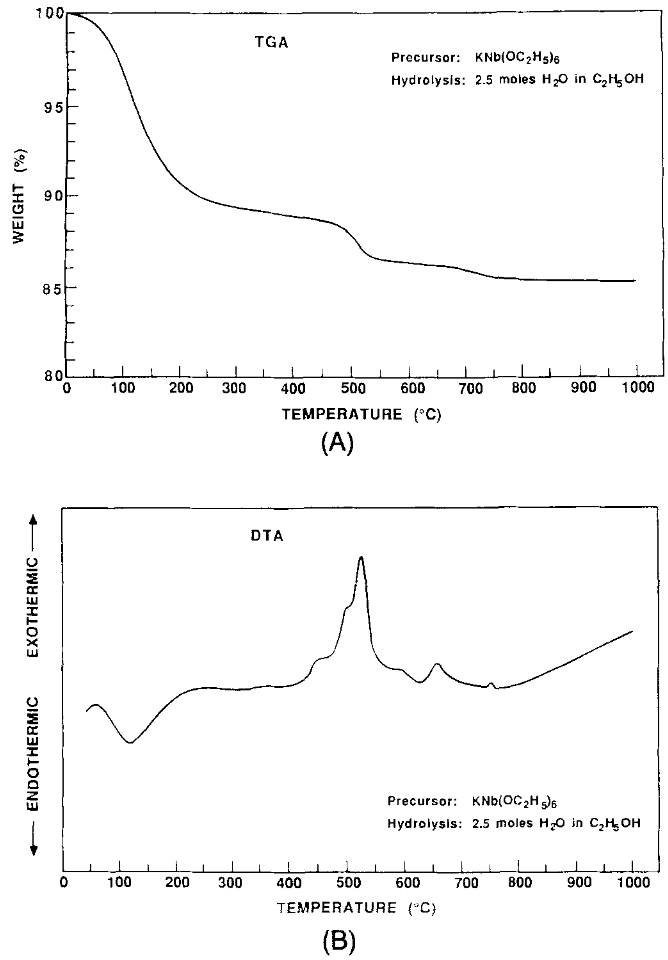

Fig. 2. (A) TGA and (B) DTA results for a sample prepared with 2.5 mol of water per mole of potassium-niobium ethoxide.

equilibrium conditions, $KNbO_3$ is orthorhombic at room temperature, tetragonal between ~225° to 435°C, and cubic at higher temperatures.[30] Figure 1 shows that the $KNbO_3$ formed by calcination at 700°C (and subsequent cooling to room temperature) retains a cubic structure[31] and does not develop the equilibrium orthorhombic phase. However, powder calcined at 800°C (i.e., above the temperature where the small exotherm in Fig. 2(B) appears) shows the development of the orthorhombic phase. This is evident in Fig. 1 from the splitting of peaks for the (100), (200), (210), (211), and (220) reflections of the cubic system.[32]

It should be noted that the small high-temperature (~750°C) exotherm was not observed for all samples. In addition, the shape, intensity, and temperature range for the strong exotherm (~420° to 550°C in Fig. 2(B)) were affected by the hydrolysis conditions (e.g., amount of water per mole of ethoxide). However, a clear relationship between the processing conditions and the DTA/TGA behavior could not be established. Chemical characterization of the residues and the volatile species formed during heat treatment would be helpful in this regard.

In order to maintain the desired $KNbO_3$ stoichiometry in powder samples, an experiment was carried out in which solvent was evaporated from the precipitated suspension, instead of being filtered. The powder was prepared using 2.5 mol of water/(mol of ethoxide), so it was still expected that potassium-deficient precipitates would form during the initial stages of hydrolysis. However, by evaporating the solvent, a potassium-rich precipitate (e.g., potassium ethoxide, potassium hydroxide) would eventually form also. It was of interest to determine if the potassium-rich and potassium-deficient precipitates would react at elevated temperature to form single-phase $KNbO_3$. Chemical analysis showed that the powder was near the desired stoichiometry after calcination at 150°C (Nb/K mole ratio = 0.94). However, the Nb/K mole ratio increased to 1.24 after calcination at 750°C, indicating that the potassium-rich precipitate volatilizes during heat treatment. This is also evident from XRD results (Fig. 3) obtained for a sample calcined at 700°C. The sample contains the same potassium-deficient phases observed in Fig. 1.

Even with low concentrations of water it was not possible to produce single-phase $KNbO_3$ when the potassium-niobium ethoxide was hydrolyzed with water/ethanol solutions. Figure 4 shows XRD results for a sample prepared with 1 mol of water/(mol of ethoxide) which was calcined at 700°C. The diffraction pattern not only contains the extra peaks observed in Figs. 1 and 3 but also has other peaks which match well with the potassium-deficient $K_4Nb_6O_{17}$ phase reported by Nassau *et al.*[29] However, it is noted that the $KNbO_3$ peaks are more intense (relative to the potassium-deficient phases) compared to the samples hydrolyzed with 5 and 2.5 mol of water/(mol of ethoxide) and calcined at the same temperature (Figs. 1 and 3).

In order to retain molecular-scale mixing and to avoid development of niobium-rich and potassium-rich precipitates, an effort was made to reduce the hydrolysis rate by using a potassium-niobium propoxide precursor. It has been noted that increasing the size of the alkoxy group decreases the rate of hydrolysis in some alkoxides.[33] This is generally attributed to steric effects. Experiments were carried out using up to 3 mol of water/(mol of propoxide). It was observed that solutions became cloudy above ~2 mol of water/(mol of propoxide). A sample prepared with 3 mol of water/(mol of propoxide) was precipitated, filtered, dried, and calcined at 850°C. XRD analysis (Fig. 5(A)) showed that the sample contained a small amount of the same potassium-deficient phases observed in Figs. 1 and 3. Samples prepared with only 1 mol of water/(mol of propoxide) remained clear during the water addition, and evaporation of solvent produced a clear gel. After drying the gel, a sample was calcined to 700°C. XRD (Fig. 5(B)) shows that single-phase $KNbO_3$ is produced, i.e., no traces of potassium-deficient phases are detected. Extensive peak splitting is observed, indicating that the orthorhombic phase can be formed using a relatively low calcination temperature.

Although single-phase $KNbO_3$ was prepared, one potential disadvantage of using propoxide precursors is that partially hydrolyzed samples may undergo larger weight loss during cal-

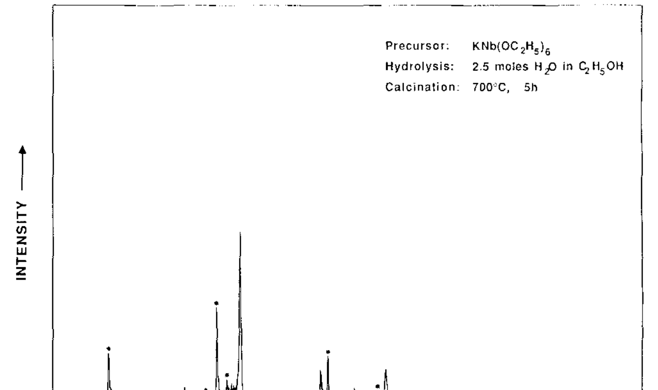

Fig. 3. XRD pattern for sample prepared with 2.5 mol of water per mole of potassium-niobium ethoxide and calcined at 700°C. Asterisks indicate that peaks are associated with potassium-deficient phase(s). Other peaks are for $KNbO_3$.

cination compared to samples prepared with the ethoxide precursors. Large weight losses can make it difficult to produce solution-deposited thin films that are free from cracks and defects. Thus, another approach investigated for preparing single-phase $KNbO_3$ involved carrying out hydrolysis of ethoxides using water/methanol solutions, i.e., instead of water/ethanol solutions. Visual observations indicated that precipitation occurred more slowly by carrying out hydrolysis with water/methanol solutions. However, a solution prepared with 1.75 mol of water/(mol of ethoxide) still became cloudy during processing. After filtering the suspension and drying, samples were calcined at temperatures in the range 650° to 850°C. XRD shows (Fig. 6) that extensive crystallization of $KNbO_3$ occurred by 650°C, with the orthorhombic phase developing after calcination to higher temperatures. However, a small amount of the potassium-deficient phases still remained after heat treatment. By reducing the water concentration to 1 mol/(mol of ethoxide), it was possible to prepare single-phase $KNbO_3$. As observed during hydrolysis of the propoxide with 1 mol of water, solutions remained clear during processing, and evaporation of solvent resulted in the formation of a clear gel. XRD analysis (Fig. 7) of samples shows

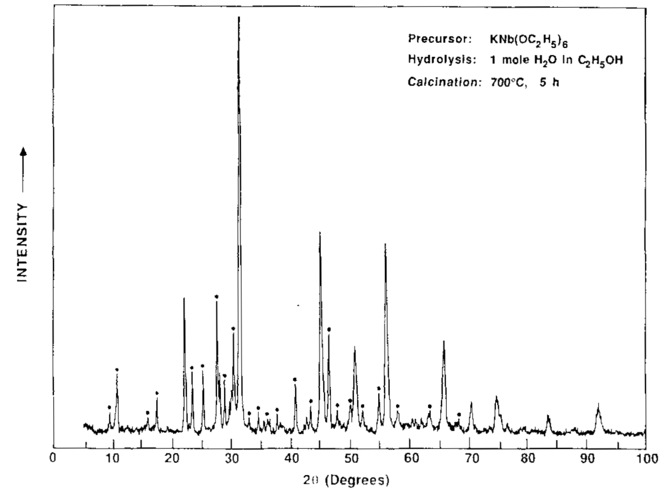

Fig. 4. XRD pattern for sample prepared with 1 mol of water per mole of potassium-niobium ethoxide and calcined at 700°C. Asterisks indicate that peaks are associated with potassium-deficient phase(s). Other peaks are for $KNbO_3$.

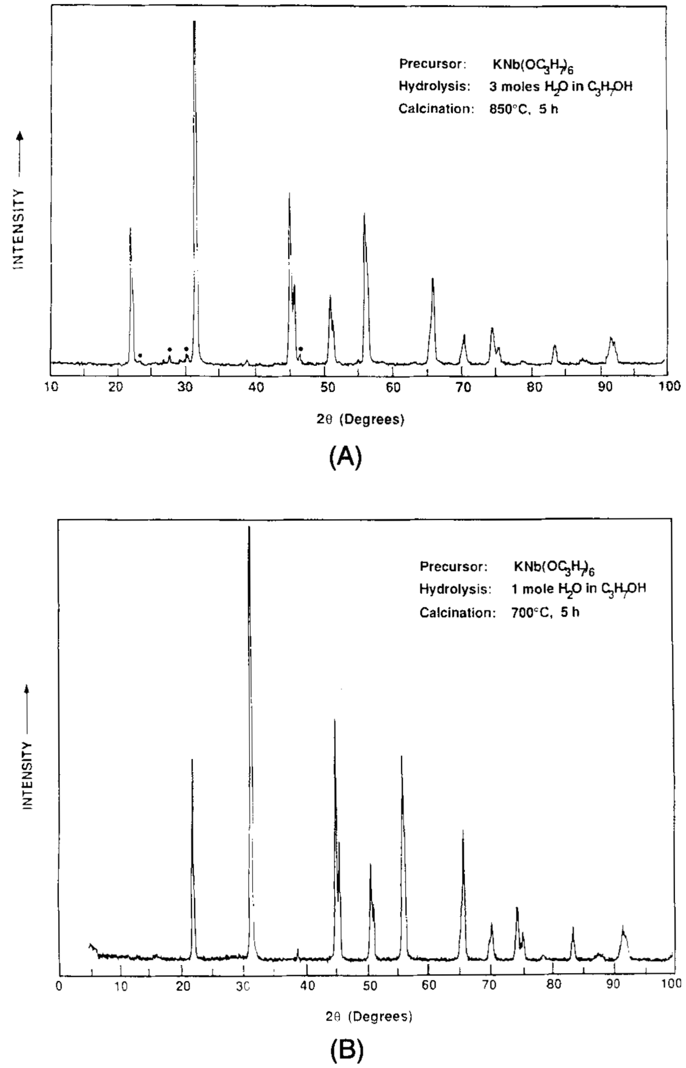

Fig. 5. (A) XRD pattern for sample prepared with 3 mol of water per mole of potassium-niobium propoxide and calcined at 850°C. Asterisks indicate that peaks are associated with potassium-deficient phase(s). Other peaks are for $KNbO_3$. (B) XRD pattern for sample prepared with 1 mol of water per mole of potassium-niobium propoxide and calcined at 700°C. Single-phase $KNbO_3$ is formed.

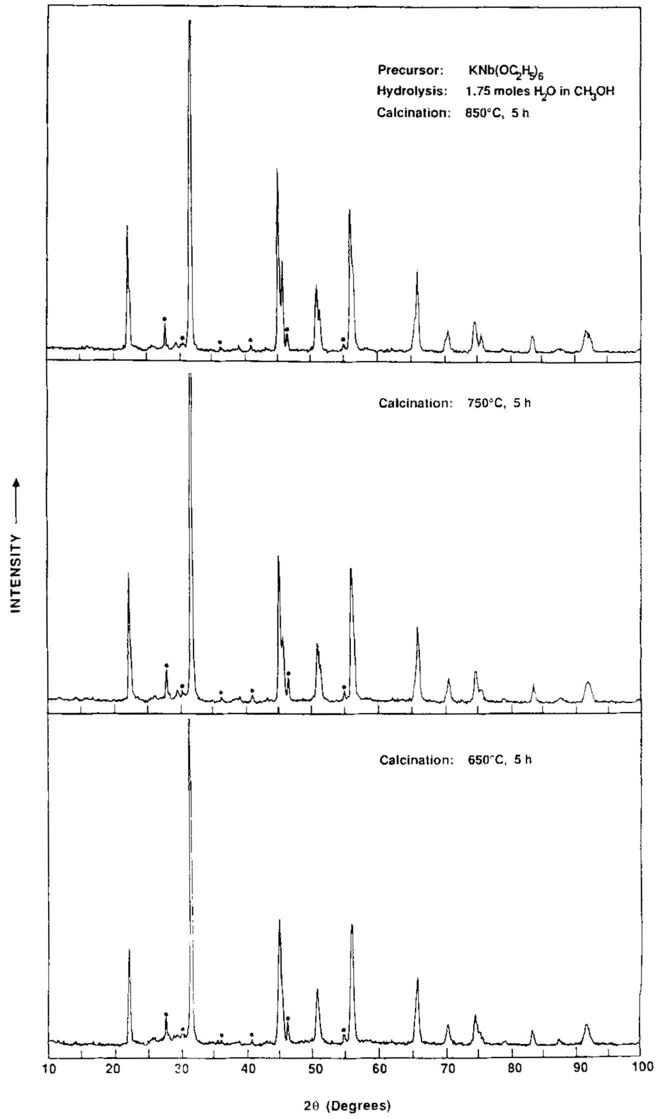

Fig. 6. XRD patterns for samples prepared with 1.75 mol of water per mole of potassium-niobium ethoxide and calcined at indicated temperatures. Samples were hydrolyzed using water/methanol solutions. Asterisks indicate that peaks are associated with potassium-deficient phase(s). Other peaks are for $KNbO_3$.

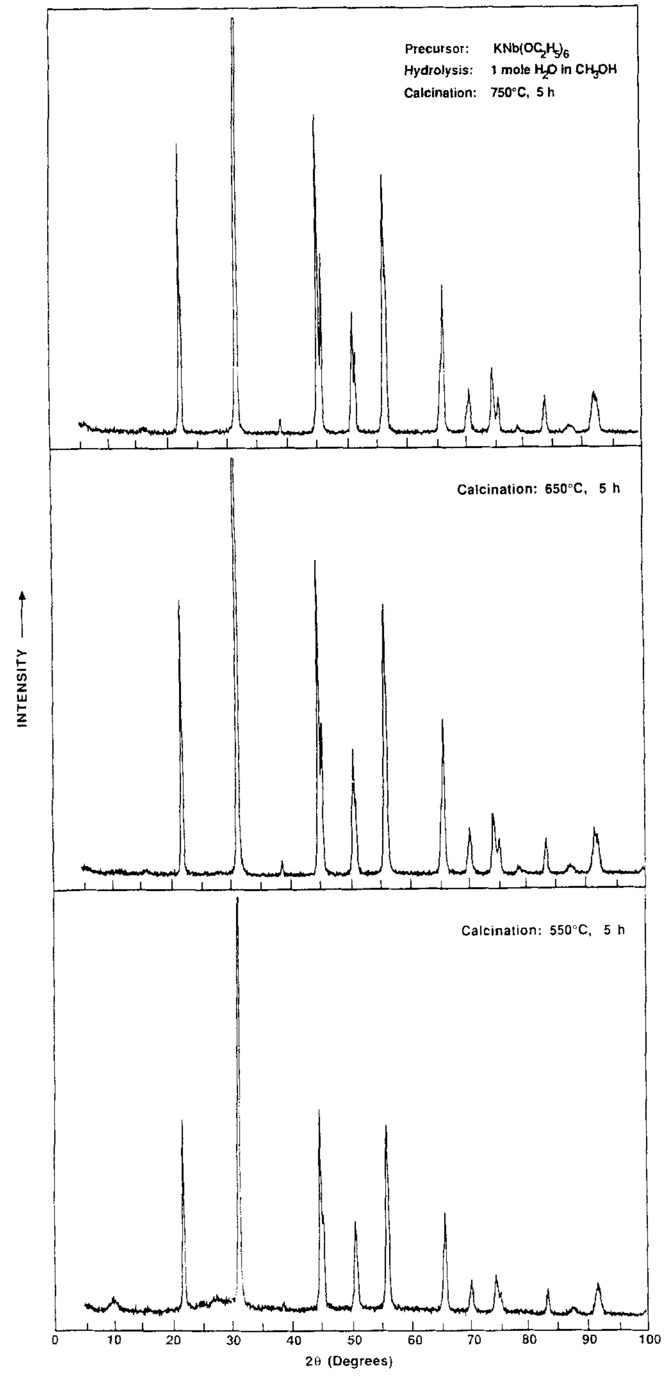

Fig. 7. XRD patterns for samples prepared with 1 mol of water per mole of potassium-niobium ethoxide and calcined at indicated temperatures. Samples were hydrolyzed using water/methanol solutions. Single-phase $KNbO_3$ is formed.

that extensive crystallization of the cubic phase occurred after calcination at only 550°C. Extensive peak splitting, indicative of the formation of the orthorhombic phase, was observed with increasing calcination temperature. Chemical analyses were also consistent with the formation of stoichiometric $KNbO_3$. A sample calcined at 150°C had 47.1 wt% Nb and 18.7 wt% K(Nb/K mole ratio of 1.06), while a sample calcined at 750°C had 52.9 wt% Nb and 22.7 wt% K(Nb/K mole ratio of 0.98). The latter concentrations also agree well with the calculated values for $KNbO_3$ of 51.61 wt% Nb and 21.71 wt% K.

The role of methanol in controlling the hydrolysis rate is not understood at this time. However, recent proton NMR results[34] have shown that addition of methanol to niobium ethoxide results in an exchange of the ethoxide group for the methoxide group. Thus, a bimetallic potassium-niobium methoxide may form when methanol is added. It is possible that this alkoxide is less susceptible (compared to the bimetallic ethoxide) to dissociation during hydrolysis. It is interesting to note that Tuttle *et al.*[23] were able to prepare single-phase $KNbO_3$ using methanolic solutions of niobium ethoxide and KOH. It is presumed that the KOH would react with methanol to form potassium methoxide and water. Except for atmospheric moisture, this reaction was the only source of water in their system during hydrolysis. Thus, the sol composition was probably similar to that used in the present study for preparing single-phase $KNbO_3$.

The clear sols prepared with 1 mol of water (in methanol) per mole of ethoxide were also suitable for forming thin films by spin coating. Single-phase $KNbO_3$ was obtained after calcination at 700°C, although peak splitting indicative of the orthorhombic phase was not observed in these samples.

IV. Conclusion

Potassium niobate was prepared by hydrolysis of metal alkoxides. Ethoxides and propoxides of niobium and potassium were initially synthesized. The single alkoxides were subsequently reacted to form the "mixed metal" alkoxides, i.e., $KNb(OC_2H_5)_6$ and $KNb(OC_3H_7)_6$. The formation of the bimetallic ethoxide was confirmed using proton NMR spectroscopy and mass spectroscopy. Additional evidence has also been obtained recently by ^{93}Nb NMR spectroscopy.[35]

Control over the hydrolysis rate of the bimetallic alkoxide was critical for preparing single-phase $KNbO_3$. High water concentrations resulted in rapid precipitation of potassium-deficient particles. After calcination, powders contained both $KNbO_3$ and potassium-deficient oxide phases. Even with low water concentration, the potassium-deficient phases could not be eliminated if the bimetallic ethoxide was hydrolyzed using a water/ethanol solution. However, single-phase $KNbO_3$ could be prepared by two methods: (1) hydrolysis of $KNb(OC_3H_7)_6$/propanol solutions using 1 mol of water (per mole of propoxide) added as a water/propanol solution and (2) hydrolysis of $KNb(OC_2H_5)_6$/ethanol solutions using 1 mol of water (per mole of ethoxide) added as a water/methanol solution. Both methods allowed the formation of stable sols and clear gels, indicating that hydrolysis/condensation reaction rates were significantly reduced. In the first method, the reactions rates are probably decreased because of steric effects arising from the larger alkoxy group in the bimetallic propoxide molecule. In regards to the second route, preliminary NMR results[34] suggest that a bimetallic methoxide may form upon the addition of the water/methanol hydrolyzing solution. Ongoing studies are directed toward confirming the formation of the bimetallic methoxide and determining if this molecule is less susceptible to dissociation during hydrolysis.

Powders prepared by the second processing route could be calcined at 550°C to form cubic $KNbO_3$ and at 650°C to form orthorhombic $KNbO_3$. It was also possible to form $KNbO_3$ thin films by this method, although the orthorhombic phase was not evident after calcination at 700°C.

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