# SYNTHESIS OF NOVEL PRECURSORS FOR PMN POWDERS AND THE THIN FILMS OBTAINED FROM THEM

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## ABSTRACT

Sol-gel processing has been widely used in the preparation of lead zirconate titanate (PZT) thin films. We have applied this methodology to the formation of lead magnesium niobate (PMN) spin-cast deposited thin films. Since there is a limited number of soluble, commercially available compounds, we have recently synthesized a series of novel metal alkoxides for use as precursors for generation of PMN thin films and powders. The process for generation of the perovskite phase of these PMN powders and films are reported.

## INTRODUCTION

The perovskite phase of lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is of interest for use in thin film capacitors and micro-electromechanical systems due to the very high dielectric constant and the electromechanical properties of PMN.[1] The perovskite phase of PMN is very disordered and considered a classical relaxor ferroelectric. A relaxor ferroelectric can be distinguished from normal ferroelectric material by several properties.[2] First, it has a broad Curie maximum point. The Curie point is the temperature at which ferroelectric material (material in which electric domains tend to be aligned parallel to one another) becomes paraelectric. For PMN this broad Curie point is reportedly due to lattice and cation disorders which result in short range order, coupled with chemical inhomogenous micro-regions.[3] Other characteristics include a diffuse phase transition and a low frequency dispersion of the dielectric constant. Single crystals of PMN have been shown to have a maximum dielectric constant of about 20,000 at 1 kHz;[2,4] however, thin film dielectric permitivities are estimated to be around 1,250 at room temperature.[3] The electrical differences have been defined by the presence of a pyrochlore phase formed during the initial stages of conversion form metal alkoxides to the ceramic form.

Sol-gel derived thin films are favored for production of PMN films due to the flexibility in the characteristics of solution precursors, the variety of deposition methodologies, and the reduction of the sintering temperatures.[5] The standard sol-gel approach to generating PMN thin films typically involves either using commercially available precursors and dissolving them in 2-methoxyethanol, which acts as both a solvent and a chemical modifier[6] or to synthesizing large metallo-organic "soap derivative" (*neo*-deconoate) compounds using organic solvents such as xylenes.[7] For the former method, water is generated as a by-product and further

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uncontrolled modifications occur. For the latter, identification of intermediates and higher organic pyrolysis temperatures are required due to the increased hydrocarbon content present. Therefore, we have developed an alternative system for fabricating PMN materials which will eliminate these two problems.

Specifically, we have synthesized lead, magnesium, and niobium alkoxide (*tert*-butoxide and *neo*-pentoxide) derivatives and utilized a magnesium alkyl reagent as starting materials. These reagents are soluble in a large number of organic solvents which do not generate the customary by-products observed in the 2-methoxyethanol based system. Due to this feature, the aging of the solution is minimal. The alkoxides we have utilized are lower in carbon content and therefore produce cleaner burnout than the "soap" derivatives. Furthermore, based on previous experience with *neo*-pentoxide complexes, characterization of the intermediate species should be possible. This paper reports the process for synthesizing the precursors and some preliminary optical and electronic characteristics of the films generated.

## EXPERIMENTAL

All reactions were performed under dry nitrogen or argon, using standard Schlenk, vacuum line, and glove box techniques. Solvents were dried and films produced as previously described.[8] Basic film processing variables were: in air deposition of 3-layers [1-layer: 3000 rpm for 10 secs., hot-plate treatment (300°C for 5 min.) repeat] followed by thermal processing [in air to 650°C, ramp rate 25°C/min., hold time 30 min.]. FT-IR data was obtained on a Nicolet, Magna System Spectrometer-550. $PbCl_2$ (Aldrich), $Mg((CH_2)_3CH_3)_2$ 1.0M in heptanes (Aldrich), and $Nb(OCH_2CH_3)_5$ (Aldrich), $NaOCMe_3$ (Aldrich) were used as received. $NaOCH_2CMe_3$ was isolated from the reaction of Na° and $HOCH_2CMe_3$ in THF and purified by sublimation.

$Pb(OCH_2CMe_3)_2$, **1**. In a Schlenk flask $PbCl_2$ (7.30 g, 26.2 mmol) is slurried in toluene (120mL). $NaOCH_2CMe_3$ (5.77 g, 52.49 mmol) is slowly added and the reaction mixture is stirred under argon overnight while heated to 60°C. The reaction is cooled to room temperature and the volatile fraction removed *in vacuo*. **1** is extracted using THF from the resulting powder. Yield 71%. FT-IR (KBr pellet) 2956(s), 2905(w), 2871(w), 2710(m), 1600(s), 1488(m), 1421(s), 1361(s), 1316(s), 1097(m), 1020(s), 955(s), 800(m), 500(w) cm$^{-1}$.

$Mg(OCMe_3)_2$, **2**. Synthesis similar to generation of **1**. $MgBr_2$ (5.0 g, 27.1 mmol), $NaOCMe_3$ (5.22 g, 54.3 mmol) in toluene (100 mL). Yield 55%. FT-IR (KBr pellet) 2961(s), 2922(m), 2899(m), 2859(m),1472(s), 1376(s), 1351(m), 1260(m), 1206(s), 1092(w), 999(s), 961(s), 921(w), 802(w), 761(w), 570(s), 494(s), 418(w), 409(w) cm$^{-1}$.

$Mg(OCH_2CMe_3)_2$, **3**. $Mg((CH_2)_3CH_3)_2$ (50.4 mL, 50.4 mmol) was syringed onto 200 mL of toluene and cooled to 0°C. $HOCH_2CMe_3$ (8.88 g, 10.1 mmol) was added by addition tube. The reaction was allowed to warm to room temperature and stirred overnight. The volatile products were removed *in vacuo*. 86.5 % Yield. FT-IR (KBr pellet) 2954(s), 2903(m), 2866(s), 2834 (m), 2791(w), 2753(w), 2720(m), 2665(w), 2615(w), 1479(s), 1464(s), 1399(s),

1362(s), 1310(w), 1258(m), 1217(w), 1094(s), 1057(s), 1027(s), 940(m), 933(m), 901(m), 801(w), 756(m), 591(s), 520(s), 447(s) cm$^{-1}$.

**Nb(OCH$_2$CMe$_3$)$_5$, 4.** In a Schlenk flask Nb(OCH$_2$CH$_3$)$_5$ (5.70 g, 17.9 mmol) is added to toluene (100 mL), HOCH$_2$CMe$_3$ (11.1 g, 89.6 mmol) is added and the reaction mixture is stirred at 60°C for 12 hours. The volatile fraction is removed *in vacuo* and the resulting off white powder can be used without further purification. Yield 44%. FT-IR (KBr pellet) 2954(s), 2902(m), 2868(m), 2693 (w), 1480(m), 1465(m), 1442(w), 1390(m), 1371(w), 1360(m), 1292(w), 1258(w), 1076(bs), 1026(s), 935(w), 918(w), 905(w), 883(m), 848(w), 803(w), 751(w), 658(s), 560(bs), 569(m), 509 (m), 482(m) cm$^{-1}$.

**{[H$_3$C(CH$_2$O$_3$)]Nb(OCH$_2$CH$_3$)$_2$}$_2$, 5.** In a Schlenk flask {[H$_3$C(CH$_2$OH)$_3$ (1.89 g, 15.7 mmol) is added to Nb(OCH$_2$CH$_3$)$_5$ (5.00 g, 15.7 mmol) in 70 mL of toluene. After stirring the reaction mixture for 12 hours, the volatile fraction is removed by rotary evaporation, washed with hexanes three times, and extracted with toluene. The resulting white powder can be used without further purification. X-ray quality crystals were grown by dissolving the extracted powder in a minimum of toluene and cooling the solution to -35°C. Yield 72% . FT-IR (KBr pellet) 2973(s), 2930(s), 2882(s), 2850(s), 2845(s), 2790(w), 2765(w), 2670(w), 1555(m), 1458(m), 1399(m), 1375(m), 1147(s), 1103(s), 1065(s), 1021(s), 1000(m) 989(s), 921(s), 620(s), 535(s) cm$^{-1}$.

## DISCUSSION

Our main goal in this project was to generate a solution that could be used to produce the ceramic perovskite phase of lead magnesium niobate (PMN). It was decided to optimize the chemical aspects of the reaction mixture (i.e., generate a soluble and stable PMN solution) before altering the processing parameters. Standard processing parameters that have been developed for lead zirconate titanate (PZT) thin films were used.[8] Since the reagents Pb(OAc)$_4$ (OAc = O$_2$CCH$_3$), Mg(OEt)$_2$ (OEt = OCH$_2$CH$_3$), and Nb(OEt)$_5$ are commercially available, we initiated our study using these reagents. A wide variety of non-reactive organic solvents were investigated, however, a homogeneous solution could not be obtained with these compounds. Acetic acid and 2-methoxyethanol are known to undergo esterification, followed by hydrolysis, and oxolation.[6,9] We chose not to investigate 2-methoxyethanol due to the toxic and teratogenic characteristics of this solvent system. Experiments utilizing acetic acid were undertaken but the commercially available components were found to be insoluble even with heating in this solvent.[6,9]

Alternative precursors were required and the number of commercially available materials is quite limited.[10] Therefore, we synthesized (Eq.1)[11] a

$$\text{MCl}_2 + 2\ \text{NaOR} \quad \xrightarrow{\text{Tol}} \quad \text{M(OR)}_2 + 2\ \text{NaCl} \qquad \text{Eq.1}$$
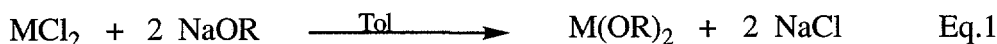
M = Pb, Mg; OR = OCH(CH$_3$)$_2$, OC(CH$_3$)$_3$, OCH$_2$C(CH$_3$)$_3$,

collection of lead, magnesium, and niobium alkoxide complexes for use in a precursor solution of PMN. The approach we used was the standard metathesis

reaction between metal halides and sodium alkoxides, simple alcoholysis exchange, or alkyl exchange. Typically these reactions were warmed slightly to insure maximum exchange had occurred. Isolation of the soluble portion generated precursors which could be used without further purification. These compounds were identified as completely as possible by FT-IR, TGA/DTA, $^1$H and $^{13}$C NMR and single crystal X-ray diffraction.

Initially we decided to utilize the bulky *neo*-pentoxide (OCH$_2$CMe$_3$) ligand since it had fewer carbons than the "soap derivatives" previously used,[7] but still maintained a similar geometric arrangement. The *neo*-pentoxide (ONep) derivatives, Pb(ONep)$_2$, **1**, and Mg(ONep)$_2$, **3**, were synthesized according to Eq. 1. Nb(ONep)$_5$, **4**, was generated by the alcoholysis exchange of NepO$^-$ for EtO$^-$ ligands. The exact number of NepO ligands substituted is still under investigation. A solution mixture which consisted of **1**, **3**, and **4** in a stoichiometric ratio of 1.1:1/3:2/3 (Eq. 2, excess lead was utilized to compensate for lead volatility which

$$Pb(OAc)_2 \ + \ 1/3\,Mg(ONep)_2 \ + \ 2/3\,Nb(ONep)_5 \ \xrightarrow{\quad THF \quad} \qquad Eq.2$$
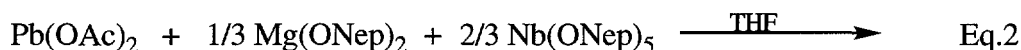
is not indicated in the equations) was attempted. **3** proved to be the limiting reagent since it is only sparingly soluble in non-reactive solvents, such as tetrahydrofuran (THF) and toluene; however, this ternary mixture was very soluble in methanol (MeOH). This solvent system would, in solution, form the methoxy derivatives and eliminate the need to synthesize a number of the above compounds. FT-IR and NMR data indicated that a complex mixture of aceto-, alkoxy complexes were generated from solutions of Eq. 2 in either solvent. Spin-cast deposited films generated from a 0.40 M THF or MeOH solvated solutions proved to be cracked and opaque. The X-ray diffraction (XRD) spectrum of the THF system indicated that the predominate phase formed was pyrochlore, similar to Pb$_{2.3}$Nb$_2$O$_{7.3}$ (see Figure 1); however, there was a substantial amount of the perovskite phase present as well. Pyrochlore is not a desirable phase of these systems since it is non-ferroelectric.[5] Exchanging Pb(OAc)$_2$ for Pb(ONep)$_2$, **1**, in Eq.2, dramatically increased the solubility of this ternary mixture. Analytical data, once again, showed a complex mixture existed in solution as well as in the solid state. XRD confirmed the formation of a perovskite phase (see Figure 1) but several unidentified peaks were present. Films produced from this mixture showed substantially less cracking and optical micrographs (1000X) looked very uniform. However, scanning electron microscopy (SEM) studies revealed a variety of defects which appeared as "blisters" and "warts" on the surface. Cross sections of this film indicated that the platinum electrode layer was "pulling away" from the TiO$_2$ adhesion layer and this is probably the cause of these defects.
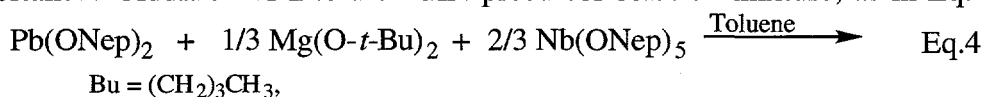
To increase the solubility of these compounds, we investigated the characteristics of the commercially available species, Mg(-*n*-Bu)$_2$, [Bu = (CH$_2$)$_3$CH$_3$)]. Addition of this species, Eq. 3, to the reaction mixture immediately

$$Pb(ONep)_2 \ + \ 1/3\,Mg(n\text{-}Bu)_2 \ + \ 2/3\,Nb(ONep)_5 \ \xrightarrow{\quad Tol \quad} \qquad Eq.3$$

$$Bu = (CH_2)_3CH_3,$$
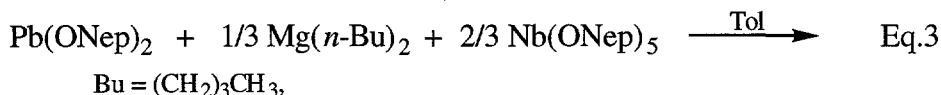
turned the solution to a dark brown color; however, no precipitate was formed initially. Based on pervious experience, this color change is a common indicator
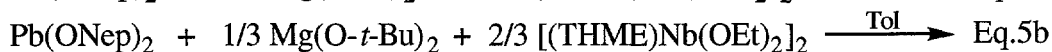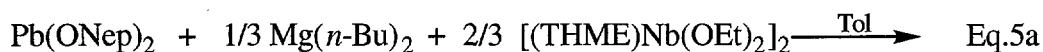
that an early transition metal alkyl has been formed. NMR data revealed a simple spectrum which was consistent with a intimately mixed species. Films generated from a 0.25 M solution of Eq.3 were transparent after initial hot-plate-bake (300°C) performed for drying and pyrolysis purposes. After firing at higher temperatures (650°C), the films showed substantial cracking and peeling. SEM studies indicated that the Pt bottom layer electrode was again being "pulled away" from the $TiO_2$ adhesion layer. XRD results on both the powder (see Figure 1) and films showed this species to be a perovskite phase of PMN similar to $Pb(Mg_{0.33},Nb_{0.67})O_3$ (peaks are slightly offset). In an attempt to reduce cracking several modifiers were added to the solution, such as: water ($H_2O$) and alcohols (ROH). Little effect was observed for these modifiers at the current level of addition; however, addition of both HOAc and acetyl acetone (Acac-H) formed gels/precipitates immediately.

It was observed that the solution generated from Eq. 3 would form a precipitate after approximately 2 hours. This was hypothesized to be due to the continued reactivity of the $Mg(R)_2$ species. Since the $Mg(ONep)_2$ complex had demonstrated low solubility, Mg species with increase solubility and decreased reactivity were desired. *Tert*-butoxide (O-*t*-Bu) ligated species possess these characteristics. Therefore, the synthesis of $Mg(O$-*t*-$Bu)_2$, **2**, as per Eq.2, was undertaken. Addition of **2** to the PMN precursor solution mixture, as in Eq. 4,

$$Pb(ONep)_2 \ + \ 1/3\ Mg(O\text{-}t\text{-}Bu)_2 \ + \ 2/3\ Nb(ONep)_5 \ \xrightarrow{\text{Toluene}} \qquad Eq.4$$

$$Bu = (CH_2)_3CH_3,$$

produced a yellow transparent solution, which upon hot-plate-bake produced a very clear film. Conversion of the organometallic species to the ceramic phase, once again, produced a film with defects; however, these faults were substantially reduced from previous attempts. Furthermore, optical microscopy (1000X) showed that the microstructure surface was very uniform; however, electrical measurements could not be undertaken due to the occurrence of electrical shorting.

A number of unique Nb compounds have also been isolated in our laboratory, one of which is $[(THME)Nb(OEt)_2]_2$, **5** [THME = $(OCH_2)_3CCH_3$]. **5** is a dimeric species both in the solid state and solution, wherein the THME ligand act as a chelating ligand to one Nb and one of the THME oxygens bridging to the other metal center. A ball-stick diagram of **5** is shown in Figure 2. **5** was introduced into the PMN precursor solution Eq. 5a and 5b to add a compound of

$$Pb(ONep)_2 \ + \ 1/3\ Mg(n\text{-}Bu)_2 \ + \ 2/3\ [(THME)Nb(OEt)_2]_2 \xrightarrow{\text{Tol}} \qquad Eq.5a$$

$$Pb(ONep)_2 \ + \ 1/3\ Mg(O\text{-}t\text{-}Bu)_2 \ + \ 2/3\ [(THME)Nb(OEt)_2]_2 \ \xrightarrow{\text{Tol}} \qquad Eq.5b$$

known nuclearity and increased steric bulk to reduce uncontrolled hydrolysis by ambient humidity. As before, the resulting mixtures from 5a turned black immediately upon addition of the $Mg(n$-$Bu)_2$. For 5b, the reaction mixture remained a pale yellow color. Films generated from 5a and b were shown by XRD to be the perovskite phase of PMN. Films from 5b demonstrated reduced cracking; however, "shorts" were reported when the electrical properties were investigated. Spin cast deposited films of 5a proved to be uniform and XRD analysis demonstrated that the perovskite phase had been formed. SEM results show very little surface defects and side views of this film showed a very densely packed material (see Figure 3). Tests of the electrical properties revealed substantial

electrical shorting occurred for a 3-layer film. Films generated by firing (650°C) between each layer proved to be extremely uniform and appeared defect-free. Electrical testing of these thin films is underway.
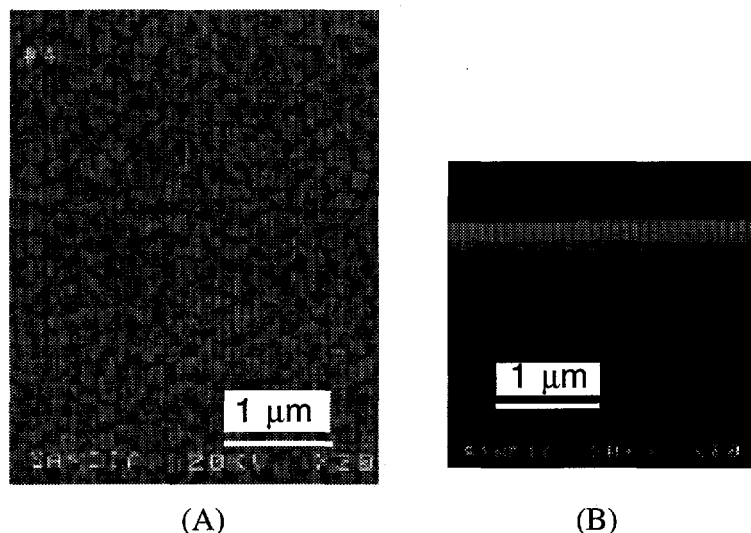


(A)                                  (B)

Figure 3.  SEM micrographs of $Pb(ONep)_2$ + 1/3 $Mg(n\text{-}Bu)_2$ + 2/3 $[(THME)Nb(OEt)_2]_2$
(A) Flat view,  (B) Side view.

## CONCLUSION

We have successfully demonstrated that from these unique precursor solutions the perovskite phase of PMN was consistently produced both in powder and thin film form.  From the variety of precursors we have synthesized and utilized, it is apparent that the more soluble and potentially "cross-linking" "$Pb(OR)_2$" and $Mg(R)_2$ type of complexes are desired for formation of the perovskite phase of PMN; furthermore, the sterically hindered $[(THME)Nb(OEt)_2]_2$ precursor is preferred versus that of $Nb(OEt)_5$.  The increase solubility insures intimate mixing whereas the steric bulk of the THME ligand insures controlled hydrolysis.  Even though thin films have been shown to be the correct phase, substantial work must be undertaken to reduce cracking of the metallo-organic phase after firing.  This will be accomplished by adding a number of potential "cross-linking" modifiers to our unique precursor solutions.  A variety of substrates and processing parameters are being investigate to determine the ideal conditions for generating defect free thin films.

## FOOTNOTES

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10. Commercially available (Aldrich) PMN precursors include: $Pb(OAc)_2 \cdot 3H_2O$, $Pb(OAc)_2 \cdot 2Pb(OH)_2$, $Mg(OAc)_2$, $Mg(OAc)_2 \cdot 4H_2O$, $Mg(OEt)_2$, $Mg(OH)_2$, $Nb(OEt)_5$.
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