NON-TRADITIONAL SOLUTION ROUTES TO FERROELECTRIC MATERIALS

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Non-traditional precursor solutions for production of ferroelectric thin films have been developed for PXZT (X = L, N, S), SBT, and PMN systems. For PXZT and SBT, pyridine is a key solvent, wherein, it both solubilizes and reduces the reactivity of the individual components of the solution. Further control of the final films has been obtained using novel tailor-made precursors to dictate their properties.

Keywords: ferroelectric materials; sol-gel; thin films; pyridine; PZT, PLZT, PNZT, PMN, SBT, alkoxide.

INTRODUCTION

Thin films of ferroelectric (FE) materials are of interest for a wide variety of electronic applications. While there are a number of methods for generating these films, solution routes have a number of advantages for preliminary studies of existing and new material systems.[1-5] Both metallo-organic (MOD) routes which utilize large "soap-like" derivatives[3,5] and the so-called "sol-gel" routes have been extensively studied.[1,2,4] The "sol-gel" routes which use 2-methoxyethanol[4] or other "chelating" reagents[2] [i.e., Inverted Mixing Order (IMO)][1]

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typically involve altering the commercially available starting materials through the use of alcohol or acid solvents at elevated temperatures.

Understanding and controlling the solution characteristics of these precursor solutions is necessary to dictate the final film properties; however, these systems are extremely complex due to chemical changes induced by the solvent/modifier and interaction of the precursors.[6] Therefore, we have studied non-traditional routes to generate "simple" (both in synthesis and reactivity) precursor solutions.

EXPERIMENTAL

Synthesis

The general synthetic process to produce precursor solutions of the "Basic Route to PXZT (PZT = $Pb(Zr,Ti)O_3$; X = La, Nb)" or BRP process[7,8], $Pb(Mg_{1/3},Nb_{2/3})O_3$ (PMN)[8,9], and $SrBi_2Ta_2O_9$ (SBT)[10] routes are illustrated in Figure 1a-c (details can be found elsewhere).[7-10] All chemicals were either used as received from Aldrich or Fisher or prepared according to literature preparations.[7-11] Lanthanum neo-pentoxide ($La(ONep)_3$) and lanthanum 2,6-bis(iso-propyl)aryloxide ($La(OAr)_3$) were supplied by Los Alamos National Laboratory.[12-14]

Film deposition

Multi-layered films of the desired composition were spin-coat deposited, in air, onto Pt-coated SiO_2/Si substrates using a photoresist spinner. After each deposition, the films were baked on a hot plate (300°C for ~5 min.) and allowed to cool to room temperature before introduction of the next layer. The SBT process requires high temperature sintering between each layer, otherwise substantial cracking occurs.[10] Precursor powders were produced by removal of all the volatile materials from the desired solutions through vacuum distillation (@ 10^{-3} Torr). Both powders and films were crystallized at the desired temperature under an air or O_2 atmosphere using a 20°C/min ramp rate.

Film characterization

Grazing incidence X-ray diffraction was used to confirm the phase purity of the final films. Scanning electron microscopy was used to examine the microstructure of the various films. In order to measure the electrical properties of the films, top platinum electrodes (150 μm in diameter) were deposited using a shadow mask to create a parallel-plate

(A)

w **Pb(L)**$_n$

L = O_2CCH_3 $n = 4$
L = acac $n = 2$

(pyridine)

x **[Zr(OR)$_4$•HOR]$_2$**
+
y **Ti(OR)$_4$**

(R = CHMe$_2$ or CH$_2$CMe$_3$)

(toluene)

w, x, y, and z = any number
(PZT $z = 0$; PLT $x = 0$)

5 minutes   5 minutes

z **Dopant**

[La(OAr)$_3$]$_2$
[(THME)Nb(OEt)$_2$]$_2$
Sn(OR)$_4$ (OR = OAr or ONp)

5 minutes

**PZT, PLT or PXZT
precursor solutions
for films and
powder production**

(B)

Pb(ONp)$_2$

(Hot toluene)

**1/3
[(THME)Nb(OEt)$_2$]$_2$**

(toluene)

60 minutes   5 minutes

**1/3
Mg(n-Bu)$_2$/Heptanes**

**PMN
precursor solution
for films and
powder production**

(C)

**Sr(OAc)$_2$
+
Ta(OEt)$_5$**

(acetic acid)

5 minutes

Bi(OAc)$_3$

(pyridine)

5 minutes

**SBT
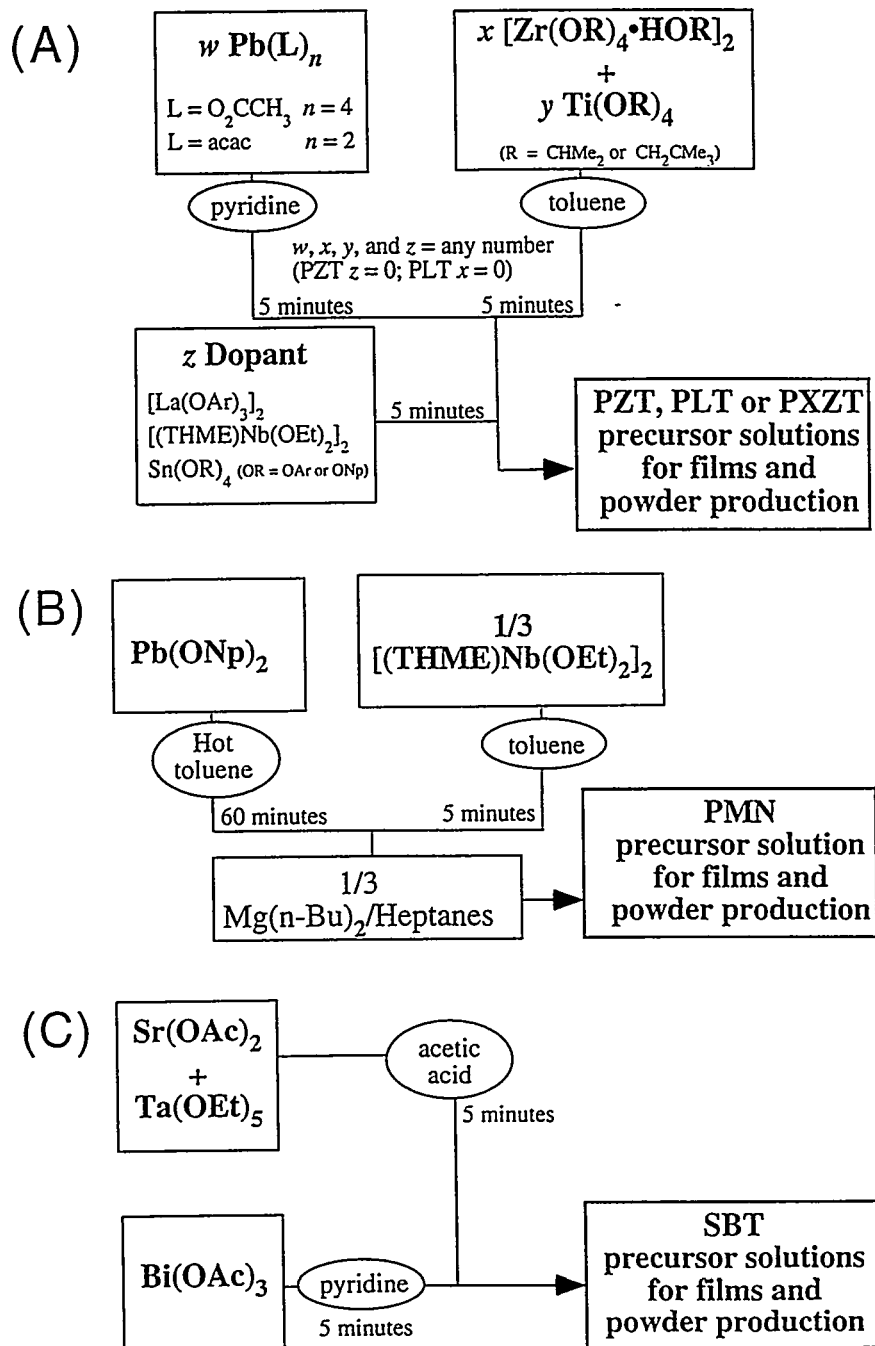precursor solutions
for films and
powder production**

Figure 1. Schematic of solution processes for:
(A) PXZT (X = L, N, S), (B) PMN, and (C) SBT.

capacitor geometry. The FE properties of the films were measured using an RT66A FE tester from Radiant Technologies. The dielectric properties were measured using an HP 4194A impedance analyzer.

RESULTS AND DISCUSSION

The IMO process (a complex HOAc/MeOH "chelate" mixture) has been extensively studied at Sandia due to the high quality PZT films that can be produced by this solution route. [6,15] In an effort to determine *in situ* generated complexes, we added pyridine (known to complex transition metal complexes and aid in crystallization) to the final IMO solution.[6,15] This resulted in the isolation of the A-site cation as $[Pb(OAc)_2 \cdot py]_\infty$ (Figure 2a) in a high yield. The B-site cation reactivity, based on the $Ti(OPr^i)_4$/HOAc model system, indicates the aging of the IMO solution[15] is due to the formation of $(Ti_6O_4(OPr^i)_{16-4n}(OAc)_{4n}$ (n = 1 or 2) and $Ti_{12}(O)_{16}(OPr^i)_{16}$ species through an esterification mechanism. Coupling this information, a solution which is (i) highly soluble, (ii) had strongly intra- but weakly interacting A and B site cations, and (iii) does not continue to react, was desired to make high quality films. We focused on using strong Lewis basic amines to increase solubility and reduce chemical reactivity.

Doped-Pb(Zr,Ti)O$_3$

The BRP process for synthesizing precursor solutions for lead containing ceramic materials incorporates these ideas. The BRP solution synthesis (see Figure 1a)[7,8] employs pyridine since it solubilizes a wide range of compounds yet it has a propensity to bind open coordination sites, reducing reactivity. Toluene was used to allow the B-site cations to intermix and to aid in wetting of the substrate. The BRP method offers several advantages over standard methods, including: rapid solution synthesis, use of commercially available materials, film production under ambient conditions, ease of dopant dissolution at high concentrations, and no heating required during solution synthesis.[7,8] Depending on the precursor, the dopant source can be added with total synthesis time < 10 min. at high concentrations.

For the lanthanum dopant, it was found that the $La(OAr)_3$[12-14] complex was rapidly solubilized at high levels. A wide variety of PLZT compositions were investigated in this study and the resultant FE properties are shown in Table 1. SEM micrographs for (a) PZT (40/60), (b) PLT (10/100), and (c) PLZT (5/30/70) thin films are shown in Figure 3a. Figure 3b shows the hysteresis loops generated from the
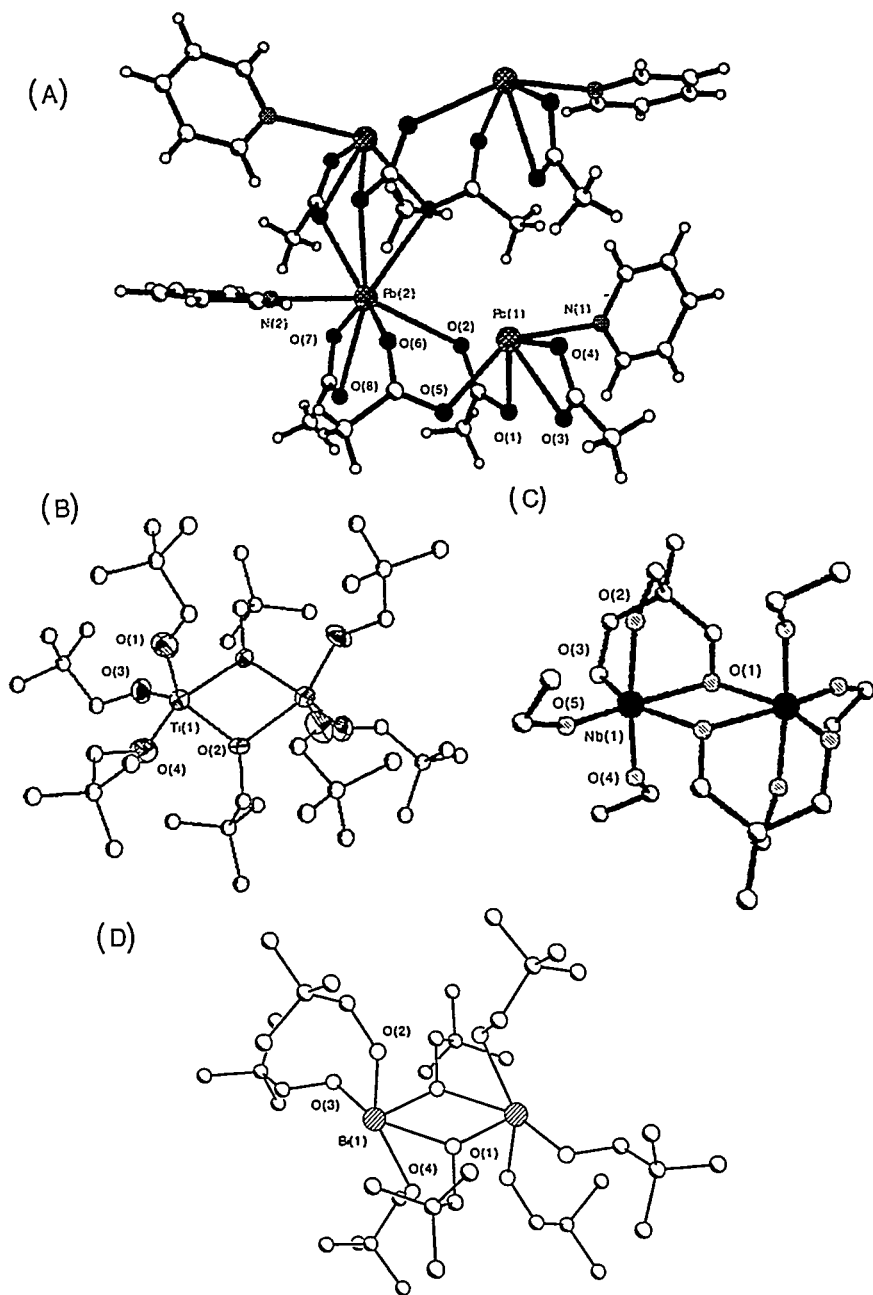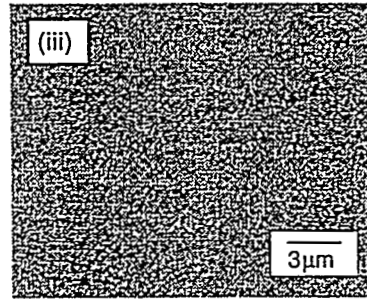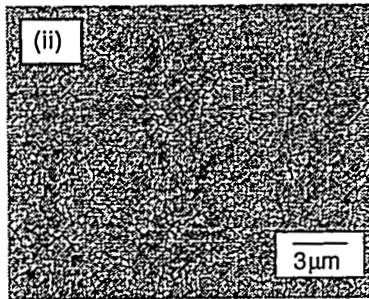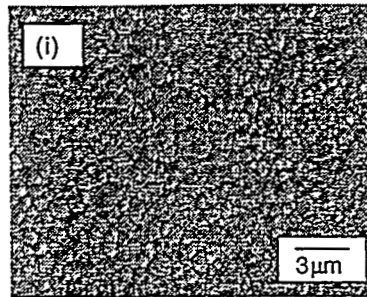
Figure 2. X-ray crystallographic structures of:
(A) [Pb(μ-OAc)(OAc)•py]$_\infty$,   (B) [Ti(μ-ONp)(ONp)$_3$]$_2$,
(C) [(μ-THME)Nb(OEt)$_2$]$_2$, and   (D) [Bi(μ-ONp)(ONp)$_2$•HONp]$_2$.
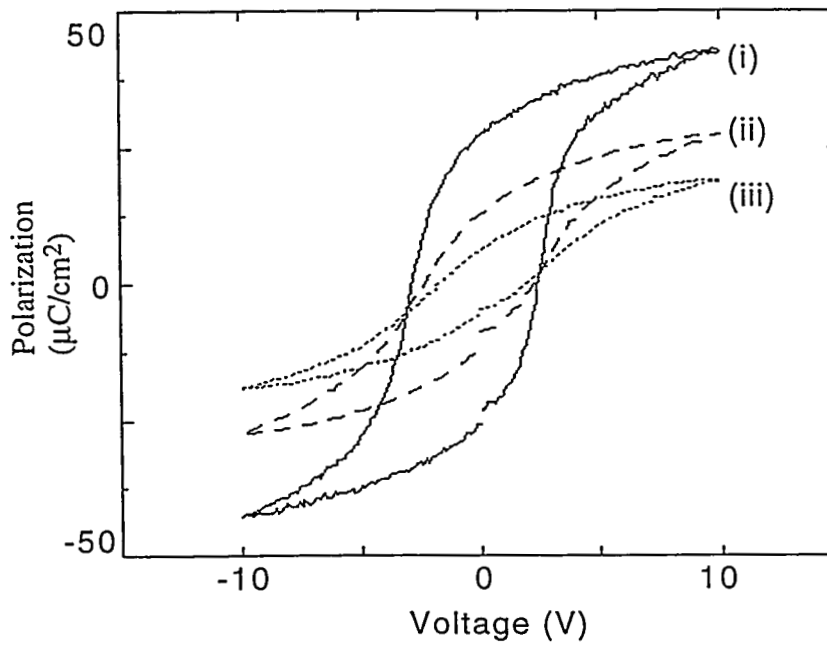
Figure 3.

(a) SEM micrographs of:
  (i)   PZT (40/60)
  (ii) PLT (10/100)
  (iii) PLZT (5/30/70)

(b) Hysteresis loops of: (i) PZT (40/60), (ii) PLZT (5/30/70), (iii) PLT (10/100).

parallel plate capacitors of these films. The FE properties of the resultant films are comparable or better than standard routes; furthermore, it is of note that the levels of doping achieved by the BRP process are not readily approachable by standard methods.

Table 1. FE properties of Electroceramic Thin Films[7,8,9]				
	~P_r ($\mu C/cm^2$)	~V_c (Volts)	~ε	~tan δ
PZT:			-	
40/60	24	5.4	743	0.027
PLZT:				
3/30/70	19	5.5	653	0.028
5/30/70	12	4.5	630	0.027
10/40/60	4.9	3.2	590	0.039
PLT:				
10/100	5.8	3.6	419	0.016
15/100	4.8	3.5	400	0.018
20/100	3.3	2.5	440	0.019
PNZT:				
4/50/50				
Nb(OEt)$_5$	18.4	5.0	981	0.072
THME-Nb	18.9	3.2	1720	0.032

A series of sterically hindered Nb precursors (4%) were introduced into the BRP process. Each compound had a different effect on the morphology and properties of the final PNZT films; however, [(THME)Nb(OEt)$_2$]$_2$ (Figure 2c) proved to be the most beneficial due to the reduced hydrolyzability of the THME ligand.[8,9] The FE properties of the THME-Nb and Nb(OEt)$_5$ (the most commonly used Nb dopant) PNZT films are shown in Table 1. All films were crystallized at 700°C and exhibit FE properties comparable to, or better than, films produced by other higher crystallization temperature methods.[8] Figure 4 a and b show the SEM and hysteresis loop of the PNZT (4/50/50) using [(THME)Nb(OEt)$_2$]$_2$ as the dopant.

We have recently demonstrated that the newly isolated and characterized, [Ti(ONp)$_4$]$_2$ (shown in Figure 2b)[11] which can be substituted for Ti(OPr^i)$_4$. Since [Ti(ONp)$_4$]$_2$ and the other BRP precursors have all been crystallographically characterized[16] and the BRP solution is "chemically simple", we have been able to undertake meaningful computer modeling. A molecular modeling approach was used to evaluate the intermolecular interactions of the organic-metal

Figure 4
(a) SEM micrographs and (b) hysteresis loop of
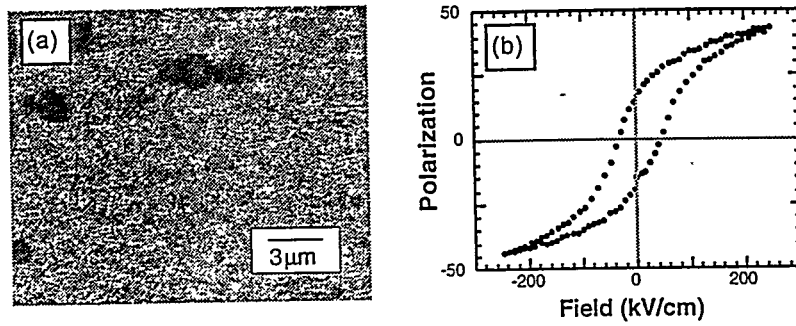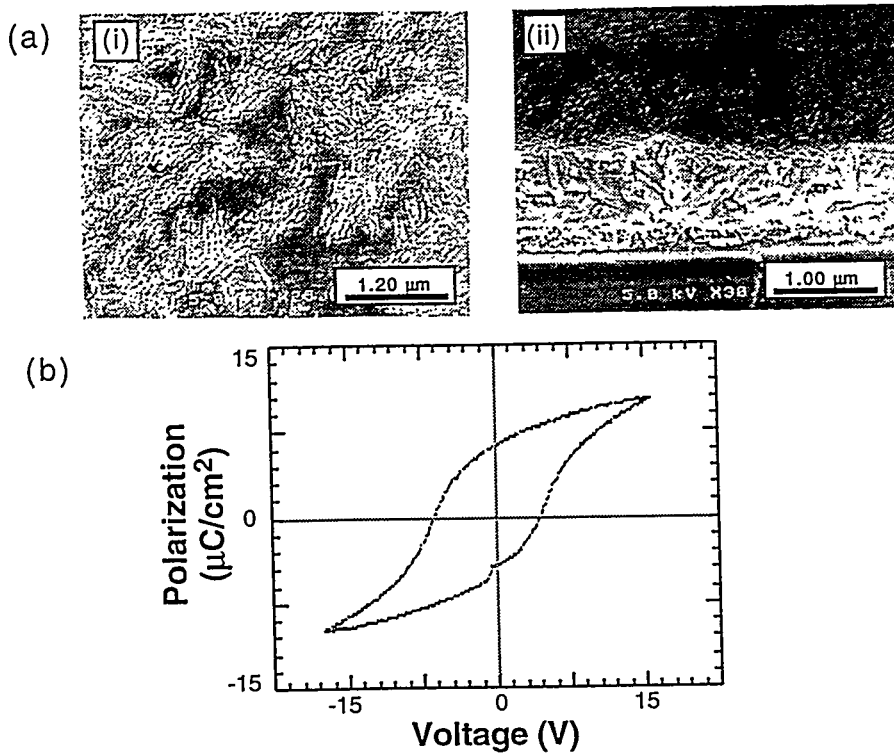PNZT (4/50/50) using [(THME)Nb(OEt)$_2$]$_2$.

Figure 5.
(a) SEM micrographs (i) top and (ii) side view and
(b) hysteresis loop of SBT fired at 650°C.

precursors expected in the preparation of the PZT precursor solutions.[17] Preliminary results based on the simulation of over a thousand-atom system (Ti-, Zr-, Pb-organic & pyridine solvent) suggest an association of the Ti and Zr precursors with the extended Pb acetate polymer.

$Pb(Mg_{1/3},Nb_{2/3})O_3$

The relaxor FE material PMN is of interest for its high dielectric constant (ε). Typically, thin films of this material has been produced by high temperature synthetic routes.[18,19] We have developed a route (shown in Figure 1b) wherein lead and niobium alkoxides are mixed in toluene and then further reacted with a magnesium alkyl solution. Once again, the $[(THME)Nb(OEt)_2]_2$ complex is the Nb alkoxide of choice.[8,9] The reaction mixture requires no heating to generate a uniform precursor solution. The solution is unstable, precipitating $Pb°$ over a 2 hour period but does generate the perovskite phase of PMN. Even in multilayered films, the interconnected nature of the porosity is apparently sufficient to generally cause electrical shorting between the sputtered top electrode metal and the continuous bottom electrode. Consequently, successful characterization of the dielectric properties of perovskite PMN films has been achieved in only a couple of cases with an effective permittivity of $\varepsilon = 800\text{-}1000$ [substantially lower than the best values reported ($\varepsilon > 2000$)].[8,9,19] Attempts to use the pyridine based process yielded a more stable solution; unfortunately, only the pyrochlore phase was formed. The reduced reactivity by the introduction of pyridine, prevents cation mixing which is thought to be necessary for the formation of the perovskite phase of PMN. This result indicates that the pyridine system is not universal for production of ceramic metal oxide materials.

$SrBi_2Ta_2O_9$

Interest in the layered-perovskite SBT stems from the reported fatigue-free switching of this material. The basic concepts of the pyridine based solution carried over to the SBT system.[10] Synthesis of the SBT precursor solution is simple, rapid (Figure 1c) and has been successfully used for the production of powders and thin films of SBT. The pyridine disrupts the polymeric $Bi(OAc)_3$, thus increasing its solubility and decreasing the reactivity of the Sr/Ta mixture. Acceptable FE properties of the SBT films could be formed at temperatures as low as 650°C, due to the lack of CO_3 formation (FTIR analysis). Testing of SBT films, fired at 750°C, reveal typical hysteresis loops with no fatigue ($> 4 \times 10^9$ cycles) and good FE properties ($P_r \sim 7.0\text{ - }8.0$

$\mu C/cm^2$; $V_c \sim 45$ kV/cm; $\varepsilon \sim 380$; tan $\delta \sim 0.030$).[10] SEM micrographs and hysteresis loops for the 650°C fired films are shown in Figure 5 a and b, respectively. Substantially better loops are produced at higher processing temperatures; however, the microstructure is not significantly altered. Newly isolated Bi containing alkoxides, $[Bi(ONp)_3 \cdot HONp]_2$ (Figure 2d) and Sr alkoxides are being introduced into this system to investigate their effects on the properties.

CONCLUSION

We have developed solution routes which utilize toluene and/or pyridine to produce PXZT, PMN and SBT.[7-10] Pyridine was chosen due to its characteristics of high solubility and reduction of precursor reactivity through the binding of solvent in open coordination sites. The resulting films of doped-PZT and SBT are of high quality and comparable to literature methodologies. In most instances we have found lower processing temperatures are obtainable for the pyridine based systems. While we have found an exception, it appears that the pyridine based BRP system is a good start for finding a general route to thin films of all materials.

Acknowledgments

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