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A new and rapid process for production of solution-derived $(Pb,La)(Zr,Ti)O_3$ thin films and powders

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A simple and rapid process for synthesizing $(Pb,La)(Zr,Ti)O_3$ (PZT, PLZT, and PLT) precursor solutions has been developed. This process, termed the ''basic route to PLZT'' (or BRP) process, offers several advantages over standard methods, including rapid solution synthesis (<10 min), use of commercially available materials, film production under ambient conditions, ease of lanthanum dissolution at high concentrations (<1 min), and no heating requirements during solution synthesis. The PLZT precursor solution synthesis involves dissolution of lead acetate (or acetyl acetate) in pyridine followed by addition of a pre-dissolved mixture of titanium and zirconium iso-propoxide in toluene. The lanthanum source can then be added and, depending on the precursor, total synthesis time was <10 min. The preferred lanthanum starting material is a highly soluble bis(iso-propyl)aryloxide complex; however, this compound is extremely air and water sensitive. The compositions investigated in this study include PZT 40/60, PLZT 3/30/70, 5/30/70, and 10/40/60, and PLT films with 10–20 mol % La. All films were crystallized at 650 °C and exhibit ferroelectric properties comparable to films produced by other techniques which require higher crystallization temperatures.

1. Introduction

Reports on various methods for the preparation of precursor solutions for the deposition of lead-containing ceramic thin films are ubiquitous in the literature [1–9]. These solution methodologies can be divided into three general categories: metallorganic decomposition (MOD), solution–gelation (sol–gel), or hybrids [1–9]. Generally, these precursor solutions utilize commercially available materials in the form of metal carboxylates and/or metal alkoxides. The majority of these methods require either synthesis of novel starting materials, relatively long mixing times, and/or heating during preparation of the desired precursor solutions. Furthermore, incorporation of lanthanum cations into the starting solutions is not easily realized, especially at higher lanthanum contents [10]. In this paper, we report a new and rapid method for the preparation of $(Pb,La)(Zr,Ti)O_3$ (PZT, PLZT, and PLT) precursor solutions of any composition [11]. This method allows solution preparation using commercially available materials (except for the lanthanum complex) and requires no heating during solution synthesis.

2. Experimental procedure

2.1. Solution preparation

The general synthetic route to generate the precursor solution, termed the "basic route to PLZT" or BRP Process is illustrated in Fig. 1. The BRP solutions were preferentially generated under dry (argon) conditions to better control the final film properties. Toluene (Aldrich) and pyridine (py, Aldrich) were dried over, and freshly distilled from, sodium naphthalide, and CaH_2, respectively. The following compounds were used as-received: lead tetra-acetate (Aldrich, $Pb(OAc)_4$), lead acetylacetonate (Alfa, $Pb(acac)_2$), titanium iso-propoxide (Aldrich, $(Ti(OPr^i)_4)$), and zirconium iso-propoxide complex (Aldrich, $Zr(OPr^i)_4$), lanthanum iso-propoxide (Alfa, $La(OPr^i)_3$), lanthanum acetate (Aldrich, $La(OAc)_3$), and lanthanum acetylacetonate ($La(acac)_3$, Alfa). The compounds 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, 13].

PZT films were made from a 0.40 M precursor solution which was synthesized by blending two mixtures. The first solution was synthesized by addition of the lead precursor [$Pb(OAc)_4$ or $Pb(acac)_2$] to pyridine, with stirring. The second mixture, prepared in a separate flask, was formed by adding $Ti(OPr^i)_4$ to

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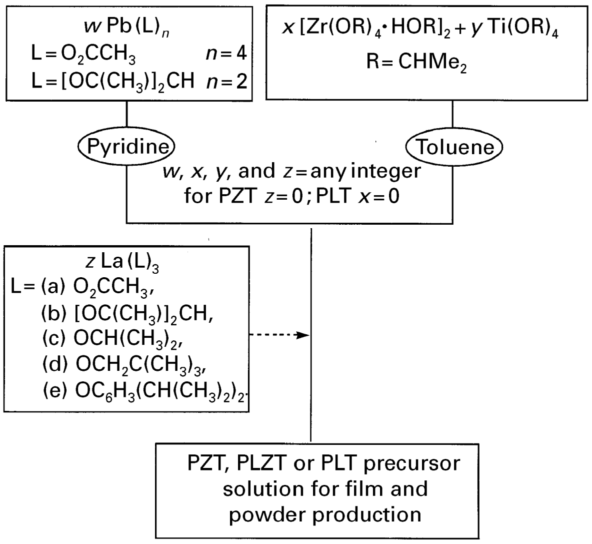


Figure 1 Process flow chart for the preparation of (Pb,La)(Zr,Ti)O_3 precursor solutions and thin films.

$Zr(OPr^i)_4$ and stirring until a slurry forms, followed by dissolution in toluene. Combining these two mixtures yielded a yellow ternary solution which was stirred until complete dissolution of the lead precursor occurs (<5 min). At this point the ternary solution was used for either film or powder synthesis.

The PLZT precursor solution was synthesized by generating a PZT solution (*vide supra*) which was followed by addition of the lathanum precursor and stirred until complete dissolution had occurred. The mixing time required to completely dissolve the lanthanum precursors without heating was ~5 h for $La(OAc)_3$, $La(acac)_3$, $La(OPr^i)_3$ and $La(ONep)_3$. In contrast, the $La(OAr)_3$ complex [12, 13] was instantly soluble at any level of doping. The preparation of the PLT solutions was analogous to that of the PLZT solutions except the zirconium precursor is omitted. Owing to the high solubility of $La(OAr)_3$ in the BRP system, it was the only lanthanum complex investigated for the preparation of the PLT precursor solutions.

2.2. Film deposition and characterization

Multi-layered films of the desired composition were spin-coat deposited, in air, on to platinum-coated SiO_2/Si substrates using a photoresist spinner (3000 r.p.m. for 30 s). 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. Precursor powders were produced by removal of all the volatile materials from the desired BRP solutions through vacuum distillation (1×10^{-3} torr; 1 torr = 133.322 Pa). Both powders and films were crystallized at 650 °C for 30 min in air using a 20 °C min^{-1} ramp rate.

Grazing incidence X-ray diffraction was used to confirm the phase purity of the final films. Scanning electron microscopy (SEM) 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 diameter) were deposited using a shadow mask to create a parallel-plate capacitor geometry. The ferroelectric properties of the (Pb,La)(Zr,Ti)O_3 films were measured using an RT66A ferroelectric tester from Radiant Technologies. The dielectric properties were measured using an HP 4194A impedance analyser.

3. Results and discussion

3.1. Solution chemistry

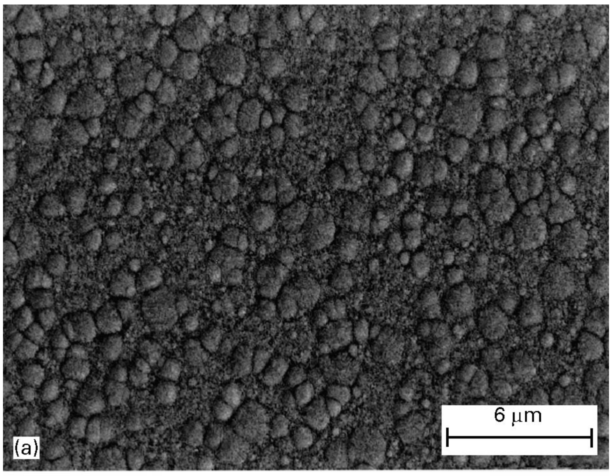
Several important results regarding the chemistry of this BRP process should be emphasized before discussing the film properties. First, owing to the high solubility of lead precursors in pyridine no external heating or complicated modifications of commercially available materials were required. Films produced using $Pb(OAc)_4$ were of higher quality than those made from $Pb(acac)_2$; therefore, all data presented are for films prepared with $Pb(OAc)_4$. In addition, all film properties presented here were measured on samples fabricated from solutions which have been prepared in a dry atmosphere. Some BRP precursor solutions were prepared under ambient atmospheric conditions, using starting materials that had been stored for long periods of time at ambient atmosphere: PZT thin films with acceptable ferroelectric properties were produced. However, it is preferable to store the precursors and prepare the solutions under dry conditions for more controllable film properties and only these films will be discussed further.

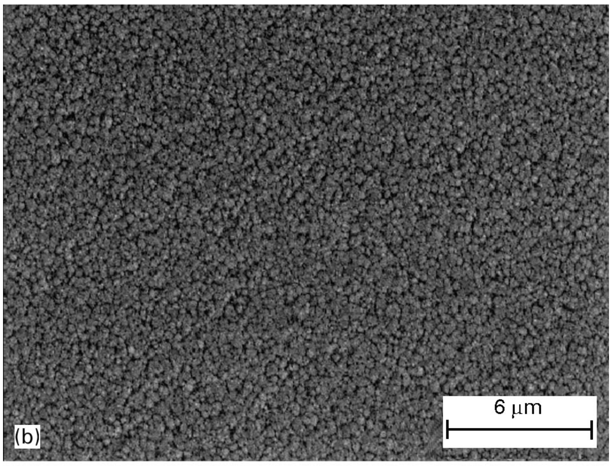
As mentioned earlier, a number of commercially available lanthanum-containing materials can be incorporated into the BRP process, without heating. These precursors include $La(OPr^i)_3$, $La(OAc)_3$, $La(acac)_3$, and $La(ONep)_3$; however, these compounds typically take over 5 h to dissolve completely in our solvent mixture. In comparison, $La(OAr)_3$ instantly dissolves, without external heating, dramatically reducing preparation times. For instance, PZT precursor solutions doped at 20 mol% lanthanum were completely synthesized in <10 min. To our knowledge, this is the first report that utilizes these types of lanthanum complexes [6] for producing (Pb,La)(Zr,Ti)O_3 materials.

Using this method, high-quality PLZT films were prepared at processing temperatures as low as 650 °C. The lower crystallization temperatures for these PLZT compositions are probably due to the combination of small ligand size, the strong Lewis basic pyridine solvent, and the rapid synthesis time. The latter two qualities, ensures limited chemical interaction between the components of the solution. This guarantees that less rearrangement is required to convert the metallorganic complexes to the desired metal oxide phase and thus lower the processing temperatures.

3.2. Film characterization

Fig. 2 shows SEMs of the PZT 40/60, PLZT 5/30/70 and PLT 10/100 films. The PZT 40/60 film appears to be non-uniform with a wide grain-size distribution that ranges from 0.1 μm to as much as 1 μm in size. In comparison, PZT 40/60 films prepared using the





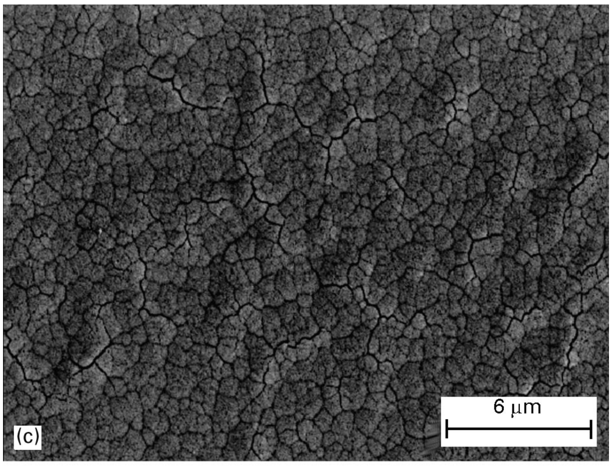


Figure 2 Scanning electron micrographs for: (a) PZT (40/60), (b) PLZT (5/30/70), and (c) PLT (10/100) thin film.

IMO process [4, 9] have smaller grain sizes (0.2 μm) and are more uniform. Despite the microstructure, it will be shown that electrical properties are comparable for the two PZT 40/60 films. PLT 10/100 thin films prepared using the BRP method have grain sizes ranging from 0.6–0.9 μm. In contrast, IMO PLT 12/100 films have ~0.1 μm sized grains [10]. The grain size of BRP PLZT 5/30/70 films is approximately 0.3 μm. PLZT films generated from the IMO process have a substantially different microstructure and are not comparable.

For the BRP method, the average grain size for the PLT 10/100 films is larger than that of the PLZT 5/30/70 films. This occurs because the increase in lanthanum content reduces the nucleation site density which increases the film's crystallization temperature. For PZT thin films it is also known that an increase in titanium content yields smaller grain sizes. This suggests that the amount of lanthanum dopant, in comparison to the titanium content, strongly influences the final grain size in the processed films.

Table I lists some of the ferroelectric and dielectric properties (i.e., remanent polarization, P_r, saturation polarization, P_s, the coercive voltage, V_c, the dielectric constant, ε, and dissipation factor, D) of various PLZT thin films produced by the BRP method. Our films compare favourably to the (IMO) [4, 9] process and other reported PLZT [1–9] processes for fabrication of high-quality PZT thin films. Listed in Table I are the properties of some analogous films generated by the IMO process, for comparison. Some trends can be discerned from these data. For instance, the

TABLE I. Electrical properties of (Pb,La)(Zr,Ti)O_3 films[a] deposited by the BRP process[b] and crystallized at 650 °C for 1/2 h in air and standard values of the IMO process[b]

Composition	Precursor method	P_r μC cm^{-2}	P_s μC cm^{-2}	$2V_c$ Volts	Dielectric constant (ε)	Dissipation factor (D)
PZT						
40/60	BRP[b]	24.1 ± 0.96	36.1 ± 2.3	5.38 ± 0.53	743 ± 49	0.027 ± 0.001
	IMO[c]	24	38	5.5	750	0.02
PLZT						
3/30/70	BRP	19.0 ± 2.0	35.6 ± 3.5	5.52 ± 0.21	653 ± 26	0.028 ± 0.002
5/30/70	BRP	12.1 ± 0.5	26.5 ± 2.7	4.45 ± 0.10	630 ± 15	0.027 ± 0.004
	IMO	13	30	4.2	750	0.02
10/40/60	BRP	4.9 ± 0.39	16.6 ± 0.1	3.22 ± 0.12	590 ± 11	0.039 ± 0.014
PLT						
10/100	BRP	5.8 ± 0.28	18.3 ± 1.0	3.64 ± 0.10	419 ± 15	0.016 ± 0.001
15/100	BRP	4.8 ± 0.62	15.4 ± 0.8	3.54 ± 0.10	400 ± 14	0.018 ± 0.001
20/100	BRP	3.3 ± 0.7	13.3 ± 0.9	2.49 ± 0.12	440 ± 28	0.019 ± 0.001

[a] All films were ~0.4 μm in thickness, 10 Volts applied for P_r and P_s measurements.
[b] This work.
[c] Refs 4 and 9.

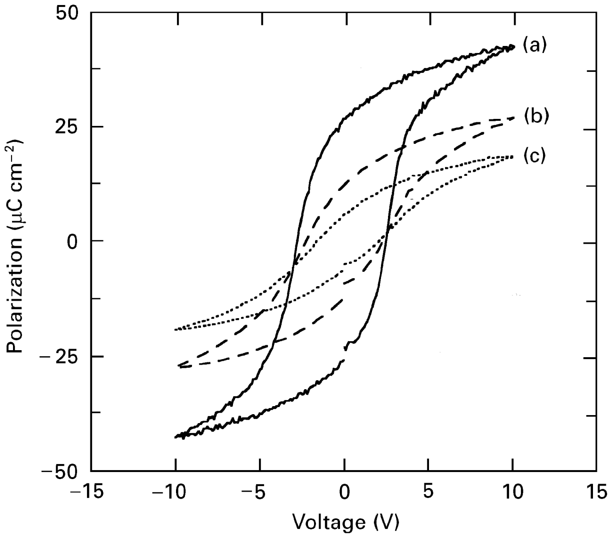


Figure 3 Typical hysteresis loop for: (a) PZT (40/60), (b) PLZT (5/30/70), and (c) PLT (10/100).

addition of lanthanum tends to decrease the coercive voltage and the magnitude of ferroelectric polarization. Fig. 3 shows three typical hysteresis curves for PZT 40/60, PLZT 5/30/70, and PLT 10/100 thin-film capacitors. As expected, the compositions containing lanthanum have slimmer hysteresis loops and lower ferroelectric polarization compared to the PZT 40/60 film, suggesting that the lanthanum component has been homogeneously incorporated into the perovskite structure.

4. Conclusion

A new, simple, quick, and reproducible method, referred to as the BRP process, for generation of precursor solutions that yield high-quality $(Pb,La)(Zr,Ti)O_3$ thin films of any composition, has been developed. All starting materials are commercially available except for the easily synthesized $La(OAr)_3$. The BRP solutions were prepared in less than 10 min, with the appropriate lanthanum precursor, and required no heating to generate the precursor solution. The perovskite phase of PLZT, PZT, and PLT films were formed using standard multi-spin coat deposition methods followed by film crystallization at 650 °C. Electrical properties of these films are comparable or better than those reported in the literature.

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