

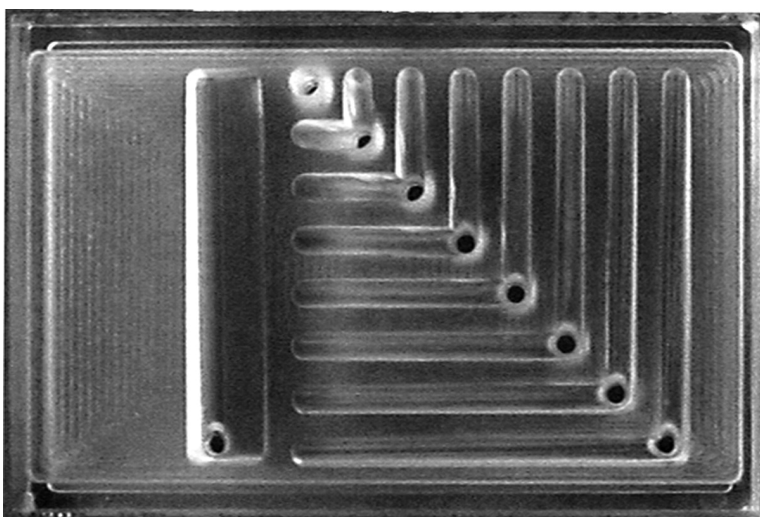
Article

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Combinatorial Synthesis of Oxide Powders with an Autopipetting System

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We describe development of a relatively simple, rapid route to produce combinatorial compositional oxide powder libraries by autopipetting of liquid precursors. This partitioning approach should apply equally well to any low viscosity, liquid precursors for the synthesis of oxide powders. A commercial autopipet is modified by fitting a plastic “mask” assembly beneath the pipet array in order to partition and direct liquids into crucibles. A series of 10 mixtures from two precursor solutions can be produced quickly. After they are dispensed, the liquid mixtures are dried in the crucibles and reacted at elevated temperatures to produce oxide powders. In the present work, the viability of the pipetting process is demonstrated by using a polymerizable complex powder synthesis method to produce $(1-x)$ LaAlO₃ – x SrTiO₃ powders. For this system, a reaction at 900 °C for 2 h in air was sufficient to yield solid solutions in this system. X-ray powder diffraction was used to determine the pseudocubic unit cell lattice parameter. The linear change of lattice constant with composition confirms the compositional accuracy of the partitioning.

Introduction

The application of the combinatorial approach has been greatly expanded upon in recent years.^{1,2} It has been applied to the study of superconductors,³ dielectrics,⁴ and photoluminescent phosphors⁵ among others. Essentially, the combinatorial approach combines automated synthesis and screening of permutations of elements. Because of the rapid, systematic production of novel compounds, it is an appealing technique to generate libraries of compounds for the discovery of advanced materials.

Many of the reported materials applications have depended on the use of thin film libraries deposited by relatively sophisticated physical vapor deposition techniques (sputtering, pulsed laser deposition, etc.). In some instances, however, small amounts of powder, or a bulk sample, are preferable to a thin film. In such a case, one needs a relatively rapid, automated means to produce appropriate samples. In a series of recent articles, Inoue and co-workers have reported development of a system for synthesis of glass powder compositions to study melting and crystallization behavior.^{6–8} Yanase et al. described a combinatorial synthesis technique based on nanoparticle slurry dispensing.⁹ In the present paper, we describe a relatively simple route to produce compositional libraries from liquid precursors by using a modified autopipettor. We demonstrate the use of this technique by employing a polymerizable complex powder synthesis method to produce $(1-x)$ LaAlO₃ – x SrTiO₃ powders.

The polymerizable complex method (PCM) of powder processing is based on the so-called Pechini process,¹⁰ wherein metal ions are suspended in solution with chelating agents (i.e., citric acid) and a polyhydroxyl alcohol (i.e., ethylene glycol). The metal ions are chelated by the citric

acid and are evenly distributed throughout the solution. Upon heating, the water or solvent evaporates, and the ethylene glycol undergoes polyesterification. Thus, a polymer resin is formed with the metal ions distributed homogeneously throughout. The resin can then be heated to higher temperatures to decompose it and form oxide powders, which typically are of high surface area (10–60 m²/gm).¹² Because the PCM is a liquid mix process, metal ions are mixed on a molecular level, so syntheses require shorter processing times and lower processing temperatures than those needed by solid state processes. For example, Kakihana et al. describe the synthesis of LaAlO₃ by this route.¹¹ In addition, the liquid mix characteristics of the process make it well-suited for automated liquid dispensing approaches. For example, we have used this approach in combination with inkjet dispensing to make catalyst libraries.¹² The present process allows larger quantities of powder to be made than by the inkjet process by virtue of the larger liquid volumes involved, which may be advantageous if, for example, pellets are needed for subsequent characterization studies.

The interest in LaAlO₃ and SrTiO₃ stems from their potential use as resonators in wireless communications applications. To be useful for resonator applications, the temperature coefficient of resonant frequency (τ_f) of a dielectric needs to be near zero. However, it is typically the case that dielectrics with high relative permittivity (ϵ_r) have a large positive τ_f . A common approach to tune $\tau_f \approx 0$ has been to combine a material with a large negative τ_f with one with a large positive τ_f . LaAlO₃ has a permittivity of 20–25 and a negative τ_f (–44 ppm/°C).¹³ SrTiO₃ has a permittivity of 180–200 and a positive τ_f (1100 ppm/°C). Thus, investigators have examined combinations of LaAlO₃ and SrTiO₃ to determine if there is a solid solution of LaAlO₃ and SrTiO₃ offering both a high permittivity value and a temperature stable resonant frequency.^{14–17}

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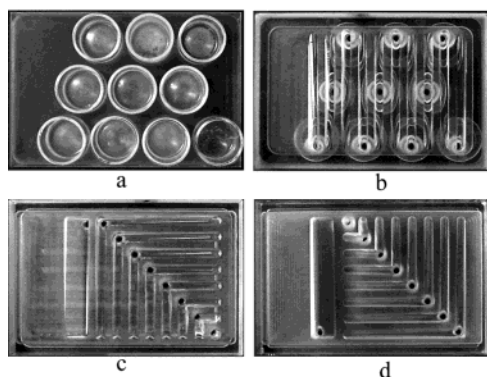


Figure 1. Top view photos of (a) bottom holder with quartz crucibles, (b) intermediate mask with channels and capture pads for crucibles, and (c,d) top masks to capture output from the 8×10 pipet tip array.

The crystal structure of LaAlO_3 exhibits rhombohedral symmetry and antiphase oxygen octahedra tilting,¹³ while SrTiO_3 adopts the ideal cubic perovskite structure. The distortion of the LaAlO_3 structure from cubic symmetry is small; hence, SrTiO_3 and LaAlO_3 are expected to form a complete solid solution. Sun et al.¹⁴ and Cho et al.¹⁶ reported on the solid solution between SrTiO_3 and LaAlO_3 . They used solid state processing, including calcining several times for durations of up to 24 h at 1350–1650 °C. In this work, we repeat their examination of the $(1-x)\text{LaAlO}_3 - x\text{SrTiO}_3$ solid solution to demonstrate the lower temperatures and more rapid processing offered by a liquid-based combinatorial approach to oxide powder synthesis. In addition, the expected linear change of the pseudocubic unit cell lattice constant with composition will serve to confirm the compositional accuracy of the partitioned compositions.

Experimental Details

The dispensing system that we developed as part of this work is based on a typical 96 well autopipetting system. We used a TomTec 96 well pipettor that can aspirate or dispense to 96 wells simultaneously. Each tip is driven by a piston that moves within its own separate stainless steel syringe body. This system is designed to dispense an equivalent amount of liquid into each well of a standard 96 well plate. As a result, we developed a “masking” system to direct varying amounts of dispensed liquid to quartz crucibles.

The pipetting system consists of a two-station shuttle, with aspiration of a liquid at one station and dispensing at the second station. For the present work, the normal $450 \mu\text{L}$ pipet tips were shortened to permit the mask assembly and crucibles to be placed underneath. The cut tips were lightly deburred and polished to minimize incomplete liquid transfer from the tip.

The purpose of the masks is to capture the dispensed liquid from the pipets and selectively route it to different crucibles. A top view picture of the mask set, machined from plexiglass, is shown in Figure 1. Figure 1a shows the bottom crucible holder with the 25 mm diameter crucibles in place. The intermediate mask (Figure 1b) consists of “gutters” that drain into holes that empty into the crucibles below. The top masks (Figure 1c or d) each consist of a 16 tip capture well (rectangular block) along with a series of angular capture

channels. Each of these channels empties into one of the gutters in the intermediate mask (panel b). In actual use then, the masks are stacked with panel a on the bottom (with crucibles in place), panel b above it, and either panel c or d on top. The masks capture the output of 80 (8×10 array) of the total of 96 pipet positions. For dispensing liquid “A”, the top mask (Figure 1c) captures the liquid dispensed by 1 (lower right corner), 3, 5, ..., 15, and 16 tips, respectively, while the intermediate mask (Figure 1b) routes the partitioned liquids into 9 of the 10 separate crucibles (Figure 1a). For dispensing liquid “B”, the top mask is replaced with a different mask (Figure 1d). Liquid B is dispensed into parts of 15, 13, 11, ..., 1, and 16, respectively, and the liquid is routed into 8 of the previous “A-containing” crucibles, plus a separate 10th crucible for the pure B. The difference between the top masks (Figure 1c,d) is a 180° rotation of both the 1–15 array and the 16 tip capture well. In the end, one is left with 10 solutions of composition 16A, 15A/1B, 13A/3B, 11A/5B, ..., 1A/15B, 16B.

As noted earlier, the PCM was used to generate the precursors dispensed with the pipetting system. A mix of 60:40 ratio of citric acid (Fisher Scientific, Fairlawn, NJ) to ethylene glycol (Fisher Scientific) was used for complexing. This composition was chosen as the result of a previous study.¹² The organic precursor solution was mixed with the appropriate metal nitrate solutions (see below) in the molar ratio of 1 mol metal to 2 mol organic to ensure complete complexing of the metal ions.

Aqueous solutions of each compound were made separately and combined with the citric acid–ethylene glycol mixture. Solutions for dispensing were made from metal nitrates, if possible, including $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Sr}(\text{NO}_3)_2$ (Johnson Matthey Company, Ward Hill, MA). The respective powders and organics were dissolved in distilled water to 0.3 M. Preparation of the La–Al precursor involved a straightforward aqueous dissolution of both nitrates along with the organics.

The Ti precursor was prepared from a Ti–peroxy complex (peroxytitanic acid) following the technique outlined by Kakihana et al.^{18,19} Ti metal powder was dissolved over a period of several hours in a cooled aqueous hydrogen peroxide/ammonium hydroxide solution, forming a yellow transparent peroxytitanic acid solution. Soon after complete dissolution of the Ti metal, an excess of citric acid with $\text{CA}/\text{Ti} = 10/1$ was introduced into the Ti solution with continuous stirring to produce a stable titanium precursor. To this solution, the Sr nitrate along with appropriate amounts of citric acid and ethylene glycol were added. As before, the solution was prepared to give an overall concentration of 0.3 M.

After the precursor solutions are prepared, the actual dispensing process takes approximately 5 min. Drying and reaction of the solutions requires another 4 h. Thus, from master batches of precursor solutions, one can produce large numbers of ~ 0.5 g samples in a relatively short time.

Results

The pipetting system was first characterized by dispensing water. To determine the amount of scatter in the system,

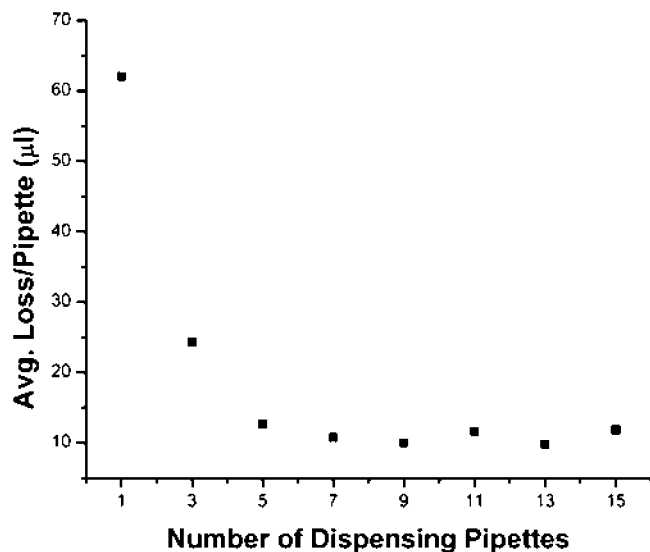


Figure 2. Plot of average pipet loss as a function of the number of pipets dispensing into a crucible.

multiple runs were performed dispensing only water. Crucibles were weighed before and after dispensing to compare the actual dispensed volume with the theoretical volume. Initially, there was substantial scatter. It was found that ridges from the machining process resulted in poor flow down the mask channels. Improvement was found with polishing of the machined channels and holes, along with the use of a surfactant (Triton X-100) to enhance surface wetting.

As can be seen from the data in Figure 2, even with these improvements, there is still significant scatter in the dispensing results. This figure shows the average loss/pipet from a 450 μL dispense. For the capture of the output of a single pipet, the loss is roughly 13%. As more pipets empty into a channel on the mask, the average loss/pipet decreases and becomes relatively constant ($\sim 2.5\%$). There is always a certain amount of liquid that remains either in the mask channels or is retained at the drip holes between the mask layers. Hence, the relative error is greater when all of the liquid is supplied from only one pipet rather than from five or more. It is likely that a more sophisticated approach to design of the masking system can eliminate much of this. For example, molding of plastic to produce higher quality surfaces along with optimally sized holes will likely reduce the losses significantly. Typically, if the property of interest was noted from a particular composition, one would validate the analysis with larger-scale synthesis (e.g., individual PCM or solid state) and further characterization.

Before synthesizing $(1-x)\text{LaAlO}_3 - x\text{SrTiO}_3$ powders, processing conditions for the postdispensing PCM powder reaction were determined. For this purpose, the LaAlO_3 precursor mixture was dried and reacted for 2 h in air over a range of temperatures from 700 to 950 $^\circ\text{C}$. The powders were then characterized by X-ray diffraction. The results of this characterization are shown in Figure 3. It can be seen that a temperature as low as 800 $^\circ\text{C}$ for 2 h is sufficient for formation of LaAlO_3 , as evidenced by high quality diffraction patterns. As has been noted elsewhere, one advantage of PCM is that it allows one to drive reactions to completion at much lower temperatures and over much shorter times

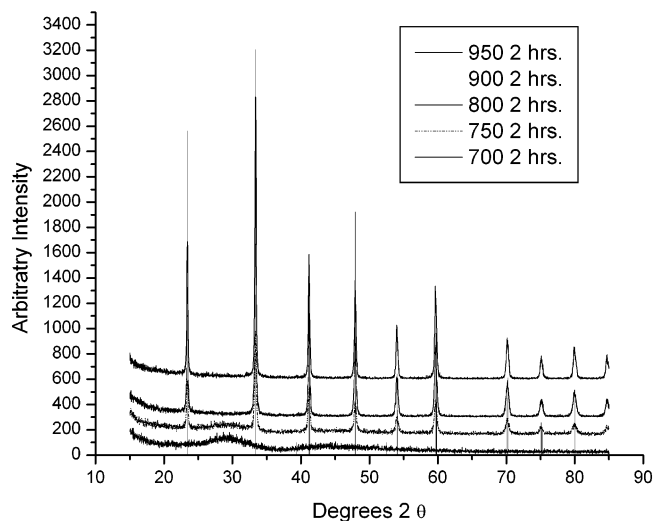


Figure 3. Diffraction patterns of LaAlO_3 powders prepared by PCM as a function of reaction temperature in air. Superimposed on the patterns are lines corresponding to LaAlO_3 from the ICDD database (31-0022).

than with solid state processing. Having established a 2 h anneal at 900 $^\circ\text{C}$ as appropriate for a complete reaction, $(1-x)\text{LaAlO}_3 - x\text{SrTiO}_3$ compositions were explored.

To demonstrate the capabilities of this autopipetting approach, the full range of $(1-x)\text{LaAlO}_3 - x\text{SrTiO}_3$ from $0 \leq x \leq 1$ was spanned with 10 compositions, and then, the $0 \leq x \leq 0.25$ and $0.25 \leq x \leq 0.50$ ranges were synthesized. To generate smaller regions of the binary composition range, the amounts deposited through the two top masks were varied. For example, to produce the $0 \leq x \leq 0.25$ series, 300 μL of LAO precursor was dispensed through one top mask, while 225 μL of LAO and 75 μL of STO were dispensed through the other top mask.

After the powders were dried and reacted at 900 $^\circ\text{C}$, the oxide powders were mixed with Si powder, which served as a reference standard for powder diffraction. The pseudocubic unit cell lattice parameter was determined (e.g., see Sun et al.¹⁴) for each of the compositions. These values are plotted in Figure 4 as a function of composition for the full range of $(1-x)\text{LaAlO}_3 - x\text{SrTiO}_3$ from $0 \leq x \leq 1$. As a reference, the values for LaAlO_3 (31-0022) and SrTiO_3 (35-0735) from the respective ICDD card files, as well as the data from Sun et al.¹⁴ and Cho et al.,¹⁶ are also shown. As seen here, similar to what was reported by Sun et al., there is a linear increase in the lattice parameter with an increase in the SrTiO_3 fraction. The corresponding sets of data for the smaller compositional ranges $0 \leq x \leq 0.25$ and $0.25 \leq x \leq 0.50$, synthesized in two separate experiments, are also shown in Figure 4.

The data follow the expected trend in lattice parameter fairly well. There is more scatter in the data from the $0 \leq x \leq 0.25$ and $0.25 \leq x \leq 0.50$ ranges than for the $0 \leq x \leq 1$. This likely reflects the smaller amount of liquid dispensed in the smaller ranges. In the $0 \leq x \leq 1$ data, 450 μL of LaAlO_3 was dispensed through one of the top masks (a), followed by 450 μL of SrTiO_3 using the other top mask (b). In producing the narrower compositional ranges, smaller amounts were dispensed, which likely accounts for some of the increased scatter.

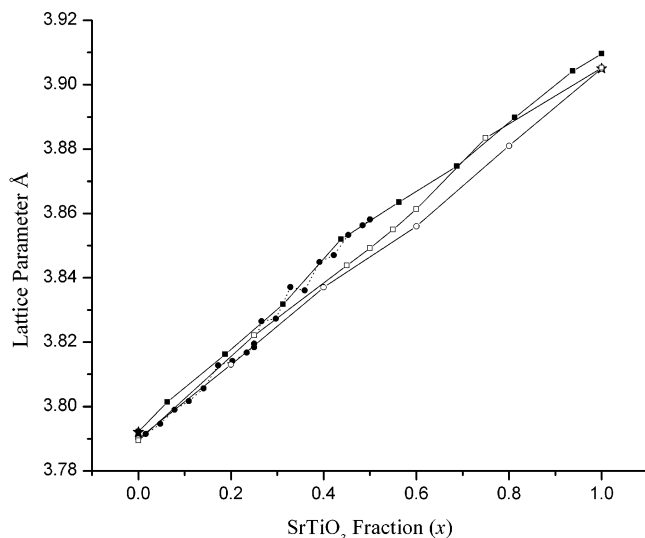


Figure 4. Plot of pseudocubic lattice parameters determined from powder diffraction. Data points marked ■ are points from full range and ● are points from $0 \leq x \leq 0.25$ and $0.25 \leq x \leq 0.50$ depositions. Other points correspond to values from the ICDD powder diffraction files (31-0022, 35-0735) as well as data from Cho et al. (○) and Sun et al. (□).

Quartz crucibles were used here because they are inexpensive and are compatible with liquids. If higher reaction temperatures are needed, chemical compatibility and crucible contamination might become a more significant issue. Depending on the chemical system being examined, ceramic crucibles (e.g., Al_2O_3) can be used instead. In addition, other liquid precursor routes for powder synthesis (e.g., sol-gel) can be employed with equal ease. Techniques other than the PCM may be more appropriate for some materials.

In the present study, the powder was intended only for characterization by X-ray diffraction. Powder samples are well-suited for catalytic studies, development of phosphors, etc., but characterization of other materials properties (e.g., conductivity, thermal expansion) may require compacted powder. For such cases, strategies need to be developed for parallel compaction of powders. Nothing is necessarily gained by increasing the speed of powder synthesis if relatively slow, serial powder compaction is still required. This merely moves the bottleneck in the process from mixing and grinding to pressing. Centrifugal casting is a technique that can be used to effect compaction of the number of vials of powder in parallel.²⁰ We have completed preliminary studies where a dispersant and binder were added to the powder after high temperature synthesis. After brief sonication, the powders were successfully compacted through centrifugation, yielding thin wafers. Obviously, such a process would have to be refined to minimize porosity and develop proper sintering protocols. However, it suggests one option to fabricate bulk samples from parallel powder processing that could develop from the rapid synthesis path described here.

Conclusions

A standard 96 well autopipetting unit was modified for use in automated powder production. With this simple system, a series of 10 combinatorial mixtures from two

precursor solutions can be produced in 5–6 h, as compared to solid state serial techniques taking 24–48 h. The technique was successfully applied to synthesis of $(1-x)\text{LaAlO}_3 - x\text{SrTiO}_3$ powders. X-ray diffraction determination of the pseudocubic unit cell lattice parameter showed the expected linear dependence with increasing SrTiO_3 content, confirming that the accuracy of the dispensed compositions falls within these analytical methods. The simple modification to an autopipettor therefore permits rapid, low temperature combinatorial synthesis of a wide range of oxide powder compositions.

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