Video Article

Bulk and Thin Film Synthesis of Compositionally Variant Entropy-stabilized Oxides

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URL: <https://www.jove.com/video/57746>

DOI: [doi:10.3791/57746](https://doi.org/10.3791/57746)

Keywords: Engineering, Issue 135, Synthesis, entropy-stabilized oxides, pulsed laser deposition, bulk ceramics, thin films, epitaxy

Date Published: 5/29/2018

Citation: Sivakumar, S., Zwier, E., Meisenheimer, P.B., Heron, J.T. Bulk and Thin Film Synthesis of Compositionally Variant Entropy-stabilized Oxides. *J. Vis. Exp.* (135), e57746, doi:10.3791/57746 (2018).

Abstract

Here, we present a procedure for the synthesis of bulk and thin film multicomponent $(\text{Mg}_{0.25(1-x)}\text{Co}_x\text{Ni}_{0.25(1-x)}\text{Cu}_{0.25(1-x)}\text{Zn}_{0.25(1-x)})\text{O}$ (Co variant) and $(\text{Mg}_{0.25(1-x)}\text{Co}_{0.25(1-x)}\text{Ni}_{0.25(1-x)}\text{Cu}_x\text{Zn}_{0.25(1-x)})\text{O}$ (Cu variant) entropy-stabilized oxides. Phase pure and chemically homogeneous $(\text{Mg}_{0.25(1-x)}\text{Co}_x\text{Ni}_{0.25(1-x)}\text{Cu}_{0.25(1-x)}\text{Zn}_{0.25(1-x)})\text{O}$ ($x = 0.20, 0.27, 0.33$) and $(\text{Mg}_{0.25(1-x)}\text{Co}_{0.25(1-x)}\text{Ni}_{0.25(1-x)}\text{Cu}_x\text{Zn}_{0.25(1-x)})\text{O}$ ($x = 0.11, 0.27$) ceramic pellets are synthesized and used in the deposition of ultra-high quality, phase pure, single crystalline thin films of the target stoichiometry. A detailed methodology for the deposition of smooth, chemically homogeneous, entropy-stabilized oxide thin films by pulsed laser deposition on (001)-oriented MgO substrates is described. The phase and crystallinity of bulk and thin film materials are confirmed using X-ray diffraction. Composition and chemical homogeneity are confirmed by X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy. The surface topography of thin films is measured with scanning probe microscopy. The synthesis of high quality, single crystalline, entropy-stabilized oxide thin films enables the study of interface, size, strain, and disorder effects on the properties in this new class of highly disordered oxide materials.

Video Link

The video component of this article can be found at <https://www.jove.com/video/57746/>

Introduction

Since the discovery of high-entropy metal alloys in 2004, high-entropy materials have attracted significant interest due to the properties such as increased hardness^{1,2,3}, toughness^{4,5}, and corrosion resistance^{3,6}. Recently, high-entropy oxides^{7,8} and borides⁹ have been discovered, opening up a large playground for material enthusiasts. Oxides, in particular, can demonstrate useful and dynamic functional properties such as ferroelectricity¹⁰, magnetoelectricity^{11,12}, thermoelectricity¹³, and superconductivity¹⁴. Entropy-stabilized oxides (ESOs) have recently been shown to possess interesting, compositionally-dependent functional properties^{15,16}, despite the significant disorder, making this new class of materials particularly exciting.

Entropy-stabilized materials are chemically homogeneous, multicomponent (typically having five or more constituents), single-phase materials where the configurational entropic contribution (ΔS_{conf}) to the Gibbs free energy ($\Delta G_f = \Delta H - T\Delta S_{conf}$) is significant enough to drive the formation of a single phase solid solution¹⁷. The synthesis of multicomponent ESOs, where cationic configurational disorder is observed across the cation sites, requires precise control over the composition, temperature, deposition rate, quench rate, and quench temperature^{7,16}. This method seeks to enable the practitioner the ability to synthesize phase pure and chemically homogeneous entropy-stabilized oxide ceramic pellets and phase pure, single crystalline, flat thin films of the desired stoichiometry. Bulk materials can be synthesized with greater than 90% theoretical density enabling the study of the electronic, magnetic, and structural properties or use as sources for thin film physical vapor deposition (PVD) techniques. As the entropy-stabilized oxides considered here have five cations, thin film PVD techniques that employ five sources, such as molecular beam epitaxy (MBE) or co-sputtering, will be presented with the challenge of depositing chemically homogeneous thin films due to flux drift. This protocol results in chemically homogeneous, single crystalline, flat (root-mean-square (RMS) roughness of ~ 0.15 nm) entropy-stabilized oxide thin films from a single material source, which are shown to possess the nominal chemical composition. This thin film synthesis protocol may be enhanced by the inclusion of *in situ* electron or optical characterization techniques for real-time monitoring of the synthesis and refined quality control. Expected limitations of this method stem from laser energy drift which may limit the thickness of high quality films to be below 1 μm .

Despite the significant advances in the growth and characterization of thin film oxide materials^{10,18,19,20,21}, the correlation between stereochemistry and electronic structure in oxides can lead to significant differences in the final material stemming from seemingly insignificant methodological differences. Furthermore, the field of multicomponent entropy-stabilized oxides is rather nascent, with only two current reports of thin film synthesis in the literature^{7,16}. ESOs lend themselves particularly well to this process, circumventing challenges that would be presented

by chemical vapor deposition and molecular beam epitaxy. Here, we provide a detailed synthesis protocol of bulk and thin films ESOs (**Figure 1**), in order to minimize materials processing difficulties, unintended property variations, and improve the acceleration of discovery in the field.

Protocol

Caution: Wear necessary personal protective equipment (PPE) including close-toed shoes, full length pants, safety glasses, particulate filtration mask, lab coat, and gloves as oxide powders pose a risk for skin contact irritation and eye contact irritation. Consult all relevant material safety data sheets before beginning for additional PPE requirements. Synthesis should be done with the use of engineering controls such as a fume hood.

1. Bulk Synthesis of Entropy-stabilized Oxides

1. Mass Calculation of Constituent Oxide Powders

1. Estimate the total desired mass of the target by multiplying the desired volume by the average density of the constituent binary oxides.

$$m_{tar} = V_{tar} * \rho_{avg}$$

$$\rho_{avg} = \sum_i X_i * \rho_i$$

where X_i and ρ_i are the mole fraction and the density of the i th component. For a 1" (2.54 cm) diameter, 1/8" (0.3175 cm) thick sample, the target volume is $\sim 1.7 \text{ cm}^3$.

2. Determine the required moles of each component by dividing this target mass by the average molar mass of the constituent binary oxides.

$$n_i = \frac{m_{tar}}{M_{avg}} * X_i$$

$$M_{avg} = \sum_i X_i * M_i$$

where M_i is the molar mass of the i th component. Convert the number of moles, n_i , back to grams by

$$m_i = n_i * M_i$$

NOTE: The masses of constituents and targeted compositions of the materials synthesized here are given in **Tables 1** and **2**.

2. Preprocessing of Oxide Powders

1. Clean an agate pestle and mortar by etching with 20 mL of aqua regia ($\text{HNO}_3 + 3 \text{ HCl}$). Pour the acid into the mortar and grind with the pestle until the bottom is clear. Dispose of the acid properly and rinse with water.
2. Combine 0.559 g of MgO, 1.103 g of CoO, 1.035 g of NiO, 1.103 g of CuO, and 1.129 g of ZnO (for equimolar composition) powders in the clean mortar.
3. Using the clean pestle, grind the powder using clockwise motions for 20 turns, then 20 counterclockwise turns. Repeat this process for at least 45 min. Use a clean metal spatula to remove powder from the sides of the mortar and brush the powder down to the center of the mortar.
NOTE: Powder mixing and grinding are complete when the powder is homogenous and grey-black in color, appears finely ground, and feels smooth.
4. Transfer the powder into a clean, sealable container for transport.

3. Ceramic Pellet Pressing

CAUTION: Wear gloves and safety glasses when assembling the die and while the press is in use. Perform entire die cleaning and assembly steps on a clean paper surface. The components used are shown in **Figure 2**.

1. Lubricate the sides and interior face of the small bottom plunger (labelled C in **Figure 2a** and **2b**) of the die with mineral oil and insert into the die cylinder until it is flush with the bottom.
2. Roll a weigh paper into the cavity of the die so that the sides of the die are covered. Pour the powder into the bottom of the die. Without allowing the small plunger to fall out of the die, gently tap the part on the counter to remove any air pockets and level the powder. Carefully remove the weigh paper.
3. Add a small amount of acetone to the powder in the cavity of the die to form a slurry. This enables grain flow while the target is under pressure and inhibits the formation of voids.
4. Lubricate the sides and interior face of the plunger (part B in **Figure 2a** and **2b**) with paraffin oil, being careful to not disturb the powder. Insert this part into the die. Place the assembled die into the pressing machine as pictured in **Figure 2c**, including the top and bottom plates (parts D in **Figure 2a** and **2b**) to provide an even surface.
5. Place die in the cold uniaxial press. Pump the press arm until 200 MPa is reached. Allow the press to sit in the compressed state for 20 min. The pressure will relax with time as the powder densifies. Add pressure as needed to maintain 200 MPa for the duration of pressing. Wipe away any excess solvent that leaks out of the die.
6. Release the press pressure. Carefully remove the top and bottom plates. Position the removal sheath and removal piston as shown in **Figure 2c**. Press slowly, removing the small die piece from the assembly before exposing the pressed target. Press the assembly carefully until the target is exposed from the die. Carefully remove the green body and transfer to a crucible for sintering.

4. Ceramic sintering

CAUTION: Target materials will be quenched from high temperatures. Wear heat resistant gloves and a face shield when removing the crucible from the hot furnace.

1. Obtain an alumina crucible that will fit the pressed powder and a 2 mm layer of Yttria-Stabilized Zirconia (YSZ) 0.1–0.2 mm beads. Coat the bottom of the crucible with YSZ beads.

- NOTE: The coating should be approximately 2 mm in thickness to ensure that the target does not contact the bottom of the crucible.
2. Slowly and carefully transfer the pressed target to the center of the crucible.
  3. Using metal tongs, carefully transport the crucible to the sintering furnace. Increase the temperature to 1100 °C at 50 °C min⁻¹. Sinter the target for 24 h at 1,100 °C in an air atmosphere.
  4. While at 1100 °C, remove the crucible from the furnace. Using tongs, quickly quench the target in room temperature water. The target will sputter for ~30 s, then remove it from the water and set to dry.
  5. Once target is cool and dry, measure the target density and compare to the theoretical value, ρ_{avg} , calculated in Part 1. Measure the mass of the target on the balance used previously, and measure the dimensions using calipers. The ratio of the measured density to the estimated value, $(\frac{m_{measured}}{V_{measured}})/\rho_{avg}$, gives the percent theoretical density.

NOTE: After the synthesis, the density is usually ~80% of the theoretical density.

6. For higher density, reground the sintered target using the pestle and mortar and repeat the Bulk Synthesis procedure from step 1.2.3. After the second sintering, determine the density of the target.

NOTE: Usually the measured density is $\geq 90\%$ theoretical density, which is suitable for pulsed laser deposition (PLD).

2. PLD of ESO Single Crystal Films

1. Target preparation

1. The bulk ceramic pellets synthesized in step 1 will now serve as deposition sources (targets). Polish the target(s) in a circular motion using progressive (320/600/800/1,200) grits of SiC paper until the surface is reflective and uniform.
2. Place the targets on the rotating carousel inside the chamber and place a ~2 cm x 2 cm piece of burn paper on the final target in the beam path.
3. Measure the laser spot size by firing a single shot at the target and measuring the resulting burn mark across both axes. If the spot size is not correct, adjust the focusing lens (**Figure 3a**). Adjust the measured spot size until an ellipse, 0.27 cm x 0.24 cm across both axes is achieved.
4. Remove the burn paper and close the door for evacuation. Evacuate the chamber using a dry scroll roughing pump to a pressure of 6.7 Pa, at which point the turbo pump can be spun up to a rate of 1,000 Hz.
5. Pump out the chamber to a base pressure of at least 1.3×10^{-5} Pa as measured by an ion gauge. Once reached, reduce the turbo to a speed of 200 Hz to allow the use of process gas during the growth.

2. Substrate Preparation

1. Clean a single crystalline, one side polished, 0.5 mm thick MgO substrate by sonication for 2 min each in semiconductor grade trichloroethylene (TCE), semiconductor grade acetone, and high purity isopropanol (IPA).
2. Blow the substrate off with ultra-dry, compressed N₂ gas, and attach the substrate to the substrate platen (**Figure 3b**) with a small amount of thermally conductive silver paint. Heat the substrate and platen to °C for 10 min on a hot plate to cure the silver paint.
3. Using the external transfer tool, place the substrate holder on the transfer arm in the chamber load lock, then seal and pump out the chamber to a pressure of at least 1.3×10^{-4} Pa.
4. Transfer the substrate into the growth chamber by opening the gate valve between the two and using the transfer arm to place the substrate platen on the heater assembly.
5. Retract the transfer arm back into the load lock and seal the gate. Lower the heater using the screw assembly on top of the chamber.

3. Laser Energy and Fluence

NOTE: Deposition is enabled by the irradiation from a 248 nm KrF pulsed excimer laser. The laser pulse width is ~20 ns.

1. Measure the laser energy using an energy meter placed in the beam path, just before entering the chamber (**Figure 3a**). Determine the mean energy after irradiating the photodiode with 50 pulses at a rate of 2 Hz.
2. Vary the excitation voltage of the laser until an average pulse energy of 310 mJ is reached with ± 10 mJ stability. Remove the energy meter from the beam path to allow the laser to pass into the chamber.

NOTE: Using a laser attenuation of the chamber window of 10%, the configuration above gives a fluence of 2.55 J cm⁻². The substrate-target distance in this work is 7 cm. A different substrate-target difference may change ideal deposition conditions and growth rate.

4. Deposition

1. Before growth, heat the substrate to 1,000 °C for 30 min at a rate 30 °C min⁻¹ in vacuum to dehydroxylize the surface of MgO crystal. Reduce the temperature to 300 °C at 30 °C min⁻¹ and allow to equilibrate for 10 min.

NOTE: Our reported temperatures are determined by a thermocouple within the heater block.

2. Flow ultra-high purity (99.999%) O₂ gas into the chamber to reach a pressure of 6.7 Pa.
NOTE: When oxygen flown into the chamber, the pressure is measured using a baratron gauge. The gas is introduced using a mass flow controller, as part of a closed loop system which stabilizes chamber pressure during growth.
3. Clean the targets of any remaining contaminants and prepare them for growth by pre-ablation. Set the selected target to raster and rotate, so that the laser is not hitting the same spot each time, ensure that the substrate shutter is closed, and ablate the target for 2,000 pulses at a rate of 5 Hz.

NOTE: The target is now prepared, and the system is at the correct conditions (temperature, pressure, fluence) for deposition.

4. Open the shutter before deposition. At these conditions, 10,000 pulses at 6 Hz produces an ~80 nm thick film.
NOTE: This growth rate was determined by X-ray reflectivity in previous work¹⁶.
5. After deposition, increase the oxygen partial pressure to 133 Pa (1.0 torr) to inhibit the formation of oxygen vacancies. Reduce the sample temperature to 40 °C at 10 °C min⁻¹. Once 40 °C is reached, close the flow of oxygen and, after the stabilization of pressure, open the gate valve between the growth chamber and the load lock. Raise the heater and use the transfer arm to remove the substrate platen from the assembly back into the load lock.

- Vent the load lock to atmosphere and remove the sample using the external transfer tool. Remove the sample from the platen using a razor blade and polish the platen to take off the remaining silver paint and deposited material. Repeat the procedure starting from step 2.2 for additional film growth.

Representative Results

X-ray diffraction (XRD) spectra were taken of both the prepared $(\text{Mg}_{0.25(1-x)}\text{Co}_x\text{Ni}_{0.25(1-x)}\text{Cu}_{0.25(1-x)}\text{Zn}_{0.25(1-x)})\text{O}$ ($x = 0.20, 0.27, 0.33$) and $(\text{Mg}_{0.25(1-x)}\text{Co}_{0.25(1-x)}\text{Ni}_{0.25(1-x)}\text{Cu}_x\text{Zn}_{0.25(1-x)})\text{O}$ ($x = 0.11, 0.27$) bulk ceramics (**Figure 4a**) and deposited thin films (**Figure 4b**). These data show that the samples are single phase and can be used in the determination of lattice constant, crystalline quality, and film thickness. X-ray photoelectron spectroscopy (XPS) (**Figure 5**) and atomic force microscopy (AFM) (**Figure 6**) data were taken to determine the nominal composition of both the targets and films and to show surface quality of the deposited thin films.

XRD spectra from the bulk ESO samples shows that the synthesized compositions are single phase rock salts with lattice parameters of 4.25 Å, 4.25 Å, and 4.24 Å for $X_{\text{Co}} = 0.20, 0.27$, and 0.33, respectively. These values are in relative agreement with Vegard's law and those reported in references 7 and 16. The lattice parameters were determined using Cohen's method²². The deposited films are single crystalline and epitaxial to the (001)-oriented MgO substrate as only the 002 and 004 film peaks are observed. The Laue fringes observed about the 002 and 004 peaks are a consequence of the high crystalline quality and smooth interfaces of the deposited films. The period of the oscillations is determined by the thickness of the film and reveals a ESO thickness of ~80 nm, consistent with our nominal thickness.

XPS data show that all constituent cations in both the ESO bulk samples and thin films are in a 2+ and high spin (where applicable) state. Compositions calculated from these spectra show that all samples are of nominal composition, to within <1% error. Compositions were obtained by fitting the XPS data to a Shirley background function implemented in CasaXPS. EDS chemical maps also agree with the nominal composition and show that the deposited films are chemically homogeneous on the length scale of 10-100 μm.

AFM micrographs show that the samples are flat across a 5 μm x 5 μm scan range with RMS roughness values of 1.1 Å, 1.2 Å, and 1.4 Å for the $X_{\text{Co}} = 0.20, 0.27$, and 0.33 films, respectively. Low angle 2θ -ω XRD data agrees with these roughness numbers¹⁶. The peak-to-peak roughness of the films is approximately 3.3 Å in all cases, which is less than the respective lattice constants of the films and may be attributed to the noise of the instrument. AFM images were processed using NT-MDT nova software.

Figure 1: Flow chart showing order of operations for entropy-stabilized oxide (ESO) thin film synthesis. First, the ESO ceramic pellets are synthesized in bulk. Then, the samples are ablated with a high-power laser and adsorbed onto a substrate to deposit single crystalline thin films. The crystallinity, topography, stoichiometry and homogeneity are proven using X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS), respectively. [Please click here to view a larger version of this figure.](#)

Figure 2: (a) Parts and (b) schematic of the pressing die. The parts are A: die, B: plunger, C: short plunger, D: top and bottom plates, E: removal piston, and F: removal sheath. (c) Picture showing the die ready for pressing. [Please click here to view a larger version of this figure.](#)

Figure 3: Schematics of pulsed laser deposition (PLD) optical path and vacuum chamber. (a) Illustration of the optical path of the PLD system and (b) cutaway view of the vacuum chamber. The beam is focused onto the target, where it excites a plasma plume that then adsorbs onto the substrate. [Please click here to view a larger version of this figure.](#)

Figure 4: 2θ - ω X-ray diffraction (XRD) spectra from as-prepared ESO samples. (a) 2θ - ω XRD spectra from as-prepared ESO bulk samples. The labeled peaks correspond to the ideal rock salt structure, showing the presence of no secondary phases. (b) XRD spectra of ESO thin films grown on (001)-oriented MgO substrates. The spectra reveal the presence of the film 001 peaks, demonstrating phase purity and epitaxy. (Inset) High resolution 2θ - ω XRD scan around the 002 film and substrate peaks, clearly showing the Laue oscillations about the film peak, demonstrating films are flat and of excellent crystalline quality. * indicates the 002 reflection from the MgO substrate. [Please click here to view a larger version of this figure.](#)

Figure 5: Composition and homogeneity of thin film ESO samples. (a) XPS of the Co variant and Cu variant ESO targets and thin films, showing that all samples are of nominal composition. (b) Energy dispersive X-ray spectroscopy (EDS) compositional maps, showing that the films are chemically homogeneous. Scale bars = 30 μm . [Please click here to view a larger version of this figure.](#)

Figure 6: Contact AFM images of the deposited Co variant (top) and Cu variant (bottom) films, showing that all films have sub-unit cell root-mean-square (RMS) roughness. The periodic pattern from top left to bottom right is an artifact of the measurement. [Please click here to view a larger version of this figure.](#)

Compound	Powder Mass (g)	Compound	Powder Mass (g)	Compound	Powder Mass (g)
$X_{Co} = 0.20$		$X_{Co} = 0.27$		$X_{Co} = 0.33$	
CoO	1.039	CoO	1.558	CoO	2.078
CuO	1.103	CuO	1.103	CuO	1.103
NiO	1.035	NiO	1.035	NiO	1.035
MgO	0.559	MgO	0.559	MgO	0.559
ZnO	1.129	ZnO	1.129	ZnO	1.129

Table 1: Masses of constituents in Co variant ESO.

Compound	Powder Mass (g)	Compound	Powder Mass (g)
$X_{Cu} = 0.11$		$X_{Cu} = 0.27$	
CoO	1.039	CoO	1.654
CuO	0.552	CuO	1.103
NiO	1.035	NiO	1.035
MgO	0.559	MgO	0.559
ZnO	1.129	ZnO	1.129

Table 2: Masses of constituents in Cu variant ESO.

Element	$X_{Co} = 0.20$ Target	$X_{Co} = 0.20$ Film	$X_{Co} = 0.27$ Target	$X_{Co} = 0.27$ Film	$X_{Co} = 0.33$ Target	$X_{Co} = 0.33$ Film
Co	0.198 ± 0.019	0.205 ± 0.024	0.272 ± 0.023	0.281 ± 0.009	0.322 ± 0.022	0.331 ± 0.028
Ni	0.199 ± 0.021	0.202 ± 0.012	0.183 ± 0.018	0.173 ± 0.017	0.172 ± 0.017	0.169 ± 0.008
Cu	0.209 ± 0.022	0.202 ± 0.018	0.176 ± 0.018	0.181 ± 0.019	0.165 ± 0.023	0.166 ± 0.012
Zn	0.202 ± 0.016	0.193 ± 0.004	0.177 ± 0.019	0.178 ± 0.016	0.164 ± 0.028	0.168 ± 0.016

Table 3: XPS determined compositions of Co variant ESO targets and thin films.

Element	$X_{Cu} = 0.11$ Target	$X_{Cu} = 0.11$ Film	$X_{Cu} = 0.27$ Target	$X_{Cu} = 0.27$ Film
Co	0.234 ± 0.016	0.232 ± 0.012	0.184 ± 0.016	0.188 ± 0.016
Ni	0.230 ± 0.010	0.229 ± 0.008	0.184 ± 0.010	0.182 ± 0.009
Cu	0.123 ± 0.010	0.125 ± 0.015	0.273 ± 0.016	0.265 ± 0.002
Zn	0.234 ± 0.016	0.235 ± 0.008	0.182 ± 0.007	0.184 ± 0.007

Table 4: XPS determined compositions of Cu variant ESO targets and thin films.

Discussion

We have described and shown a protocol for the synthesis of bulk and high-quality, single crystalline films of $(\text{Mg}_{0.25(1-x)}\text{Co}_x\text{Ni}_{0.25(1-x)}\text{Cu}_{0.25(1-x)}\text{Zn}_{0.25(1-x)})\text{O}$ ($x = 0.20, 0.27, 0.33$) and $(\text{Mg}_{0.25(1-x)}\text{Co}_{0.25(1-x)}\text{Ni}_{0.25(1-x)}\text{Cu}_x\text{Zn}_{0.25(1-x)})\text{O}$ ($x = 0.11, 0.27$) entropy-stabilized oxides. We expect these synthesis techniques to be applicable to a wide range of entropy-stabilized oxide compositions as more are discovered in the development and expansion of the field. Further, the synthesis of compositionally varied entropy-stabilized oxides offers a platform for studying the roles of structural and chemical disorder on functional properties.

While our protocol leads to single phase and high-quality entropy-stabilized oxides, limitations to the technique exist and modifications to the synthesis can be envisioned for advanced understanding of the material and higher reproducibility of the synthesis. Below, we outline critical steps within the protocol, possible modifications, troubleshooting and limitations of the technique, the significance with respect to existing methods, and envisioned future applications for this technique. Critical steps to this process are sintering, quenching, the dihydroxylation of the MgO surface, and the determination and monitoring of the laser fluence. For the bulk samples to be single phase, it is essential that they are sintered for at least 24 h and rapidly quenched from the sintering temperature. If the bulk targets are not single phase, or of the desired density, they can be reground and repressed to reach a higher density. The dihydroxylation of the MgO surface is also a critical step, as attempts to grow on (001)-oriented MgO without this result in amorphous films. Another key issue and limitation of the technique includes the drifting of the laser energy leading to deviation from the intended deposition conditions. This is discussed more in depth below.

The modifications to the technique increase reproducibility and enable real-time troubleshooting. In particular, *in situ* analysis, such as reflection high-energy electron diffraction²³ (RHEED), low-angle X-ray spectroscopy²⁴, X-ray reflectivity²⁵, X-ray diffraction^{26,27}, second harmonic generation^{28,29}, or ellipsometry³⁰, can be added to the thin film deposition procedure. This would enable structural and compositional characterization for real-time monitoring of the thin film growth conditions. As our protocol does not involve any *in situ* diagnostics, our report of potentially critical surface kinetics and structural evolution, that may occur during synthesis, is lacking. Further, our protocol calls for the constituent powders to be hand mixed and grounded with an agate mortar and pestle. Others in the community, however, have reported the use of shaker⁷ and ball milling¹⁵, using YSZ or agate media, which may give more consistent results by eliminating the physical demand of hand grinding.

The method outlined produces films of excellent quality, however, there are several inherent limitations to the technique. PLD makes it challenging to grow films significantly beyond 1 μm of thickness due to the drift of the laser energy. Drift of the laser energy can occur due to the passivation of F_2 gas in the excimer laser tube with time and excitation of the gas. Further, laser energy drift can occur from material deposition on the UV transparent laser window on the chamber (**Figure 3b**). Our protocol reports the deposition on ~80 nm thick films using an oxygen pressure of 6.7 Pa; before and after this growth, we do not observe a change in the transmission of the UV laser window, which has ~10% intrinsic attenuation³¹. This may be a result of the relatively high oxygen pressure used during deposition, the relatively low number of shots, and the geometry of our deposition chamber. The depositions of films of appreciably larger thicknesses, with lower reactive gas pressure, or different laser window position with respect to the target may encounter difficulties stemming from laser energy drift. Energy drift due to the passivation of F_2 gas in the laser tube can be minimized by routinely filling with fresh gas and monitoring the energy reported by the internal laser energy meter during deposition to compensate a decrease of laser energy with an increase in excitation voltage.

Entropy-stabilized oxides tend to have five or more cations where the entropy and bulk stabilization temperature depend drastically on composition. While currently no other deposition method has been reported to successfully grow entropy-stabilized oxide thin films, the stoichiometric evaporation and transfer from the target in PLD^{16,32} may provide the best chemical homogeneity. For instance, MBE and sputtering are alternative physical vapor deposition techniques that can be used to deposit high quality thin films^{33,34}, however, MBE and multiple target co-sputtering would require accurate calibration and stable flux from five individual sources. This task is cumbersome and illustrates the anticipated difficulty in establishing the chemical homogeneity throughout the deposition of the film, assuming these techniques can be proven to deposit entropy-stabilized materials. Further, as the bulk materials require quenching from high temperature to maintain the entropy-stabilized phase, a significant density of thermodynamic point defects may prevent accurate determination of lattice parameter, resistivity, and dielectric properties. In theory, PLD should provide the ability to control the density of such defects³⁵ and enable the accurate determination of functional and structural properties. Thus, the methodology presented here is significant for the investigation of the novel and giant functional properties of these materials.

Disclosures

We have nothing to disclose.

Acknowledgements

This work was funded in part by National Science Foundation grant No. DMR-0420785 (XPS). We thank the University of Michigan's Michigan Center for Materials Characterization, (MC)², for its assistance with XPS, and the University of Michigan Van Vlack laboratory for XRD. We would also like to thank Thomas Kratoch for his assistance with bulk materials preparation.

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