Research Statement

Novel Complex Oxides: From Synthesis to Tunable Functionalities

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Prospective—Complex oxides offer an extremely wide range of functional properties compared to conventional metallic alloys or compound semiconductors [1]. At Texas Tech University (TTU), I propose to develop a research theme focused on the design and synthesis of novel complex oxides aimed at discovering, understanding, and engineering these materials for next generation computing, sensing, and energy applications.

Research Background

My research interests involve design and synthesis of novel complex oxide thin films and heterostructures and their multiscale characterizations to exploit and control novel physical properties and functionalities which are not present in bulk materials. My Ph. D. and postdoctoral research work involved; Pulsed laser epitaxy (PLE) growth of functional complex oxide thin films and the use of scanning probes, structural probes, advanced scattering techniques as well as macroscopic characterizations to study dielectric, ferroelectric, piezoelectric, magnetic, and correlated-electron properties (**Figure 1**).

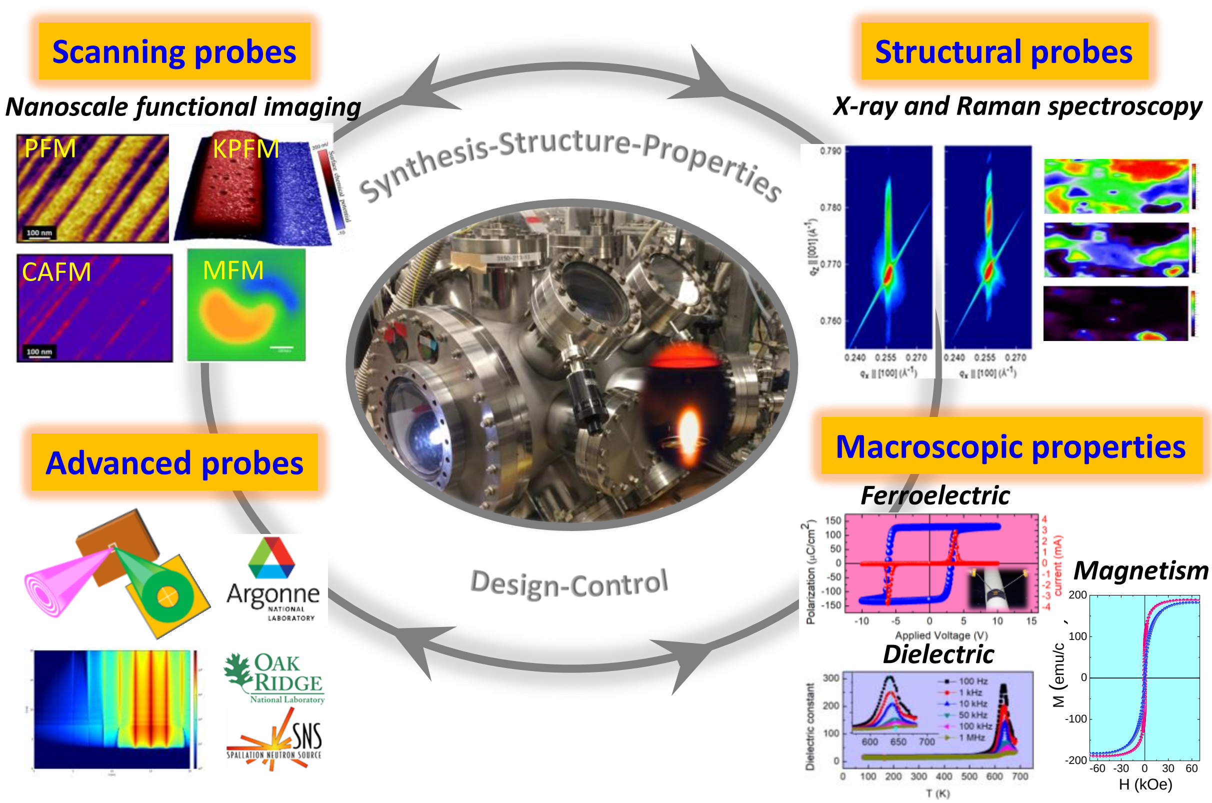

Figure 1. Design and synthesis approach focused on discovering novel complex oxide nanostructures using pulsed laser epitaxy and utilizing multi-scale characterization techniques to understand and engineer the functional properties.

Research Plan

As highlighted in **Figure 1,** with my expertise on PLE growth and multi-scale characterizations of functional oxide thin films, I plan to build my research laboratory based on the programs detailed below:

Program 1: Entropy Stabilized Oxides (P 1)—Synthesis of single-crystal high-entropy oxide epitaxial films to study the effects of chemical disorder on emergent functionalities.
Program 2: Lead-Free Ferroelectric Oxides (P 2)—Discover and study environment-friendly lead-free ferroelectrics.
Program 3: Oxide Electronics (P 3)—Utilize complex oxide thin films and heterostructures for advanced electronic applications.

These projects will synergistically include the experimental (*Profs. Duncan and Peralta*) and theoretical groups (*Profs. Sanati, Myles, and Estreicher*) within the Department of Physics and Astronomy. The diversity of these research programs will create possibilities to establish interdisciplinary collaborations with other departments (*Chemistry, Chemical Engineering, and Electrical and Computer Engineering*) and major research centers (*NTC and HPCC*) at TTU.

P 1: Endowing New Functional Oxides—Advancing fundamental knowledge to design and control epitaxial complex oxides, I will lead efforts to synthesize epitaxial thin films and heterostructures of the high-entropy oxides (HEOs)—promising materials system to open many new functional opportunities not possible in traditional high entropy metal alloys [2]. This class of functional materials could be fundamentally and industrially important, offering a wide-range of opportunities for various electronic and quantum applications, such as sensors, quantum information, memory, and energy storage.

To begin, I will focus on synthesis of the bulk ceramic HEOs in ABO_3–perovskite and AB_2O_4–spinel structures using conventional solid-sate reaction method. In second step, using these ceramics as target materials, I will grow epitaxial thin film using PLE. The HEOs have hardly been explored as high-quality epitaxial thin films [3]. PLE is shown to be an effective route to obtaining high-quality single-crystal HEO thin films, which will enable me to achieve a trajectory for leadership in this research field. Utilizing an entropy-stabilization-approach, I will grow the epitaxial thin films of these oxides imposing different strain-states and study the structure-properties relation using high-resolution X-ray, scanning transmission electron microscopy, scanning probe microscopy, and transport measurements.

Figure 2 shows an example of synthesized single crystal high entropy perovskite oxide (HEPO) film by stabilizing the multicomponent $A(5B_{0.2})O_3$ perovskite $Ba(Zr_{0.2}Sn_{0.2}Ti_{0.2}Hf_{0.2}Nb_{0.2})O_3$ epitaxially on $SrTiO_3$ and MgO substrates by our team at ORNL [4]. The selection of B-site sublattice substitution is motivated by the strong impact of the oxidation state and bond lengths (O-B-O and B-O) of the B-site cations to the perovskite functionality. The HEPO films show extremely low thermal conductivity and relaxor-ferroelectric behavior near room temperature. These oxides are ideal materials for gate dielectrics, energy storage capacitors, nano- and micro-electromechanical systems, and piezoelectric sensor applications [5]. Moreover, the ability to

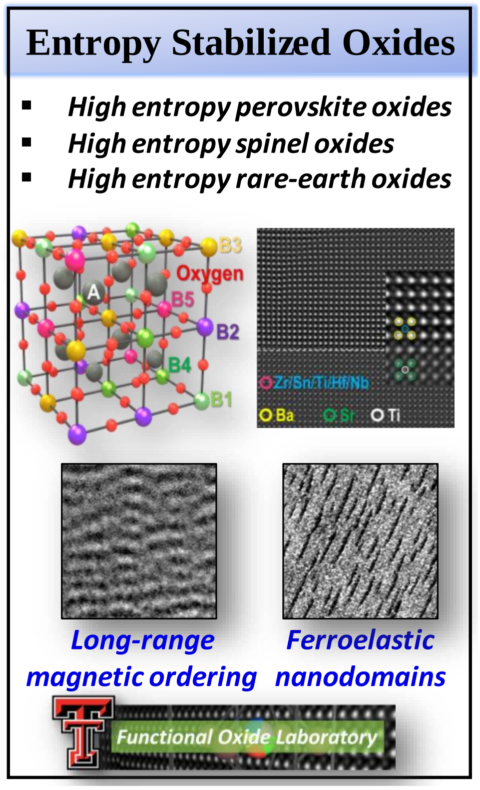

Figure 2. Designing novel functionalities through understanding and controlling chemical disorder in high entropy oxides' epitaxial films.

select designer combinations of A or B-site stoichiometries might offer new potentials to modifying functionalities and will likely lead to unprecedented disorder-driven physical phenomena. This project will require use of synchrotron and neutron beam-line-based measurements. I will be writing proposal for beam-time at APS, Argonne (for soft/hard X-ray measurements) and SNS-HIFR, ORNL (for neutron diffraction studies). *Based on my expertise using PLE, I intend to use and develop pulsed laser deposition facility at physics department which will provide fundamental insight required for design of new functional nanomaterials and will initiate new collaborative projects between TTU and other research institutions.*

P 2: Novel Lead-Free Ferroelectric Oxides—Developing functionally capable clean, green, and non-toxic materials is important to all of us. As an example, green ferroelectrics/piezoelectrics are required for various real-world applications. I will focus on synthesis of environmental benign polar perovskite oxides and study their ferroelectric, dielectric, and piezoelectric properties. As highlighted in **Figure 3**, I will focus on the PLE synthesis of tin titanate–$SnTiO_3$ perovskite. In addition, I will plan to synthesize other ferroic oxide systems, such as rare-earth orthochromites ($RCrO_3$) and orthoferrites ($RFeO_3$).

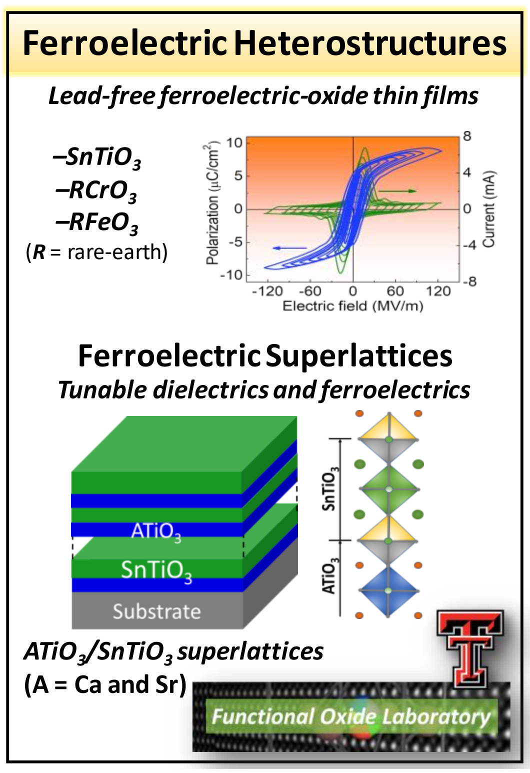

Figure 3. The atomic-scale growth control of novel ferroic-heterostructures and superlattices with tunable properties.

I will synthesize tin titanate–$SnTiO_3$ perovskite oxide, which has been reported to be a room-temperature ferroelectric with large spontaneous polarization and lower optical band gap compare to $BaTiO_3$ [4,5]. However, the origin of ferroelectricity is ambiguous, and controlled synthesis of ferroelectric-phase has not been realized yet [7,8]. I will develop the synthesis of $SnTiO_3$ ceramics and study the structure-property relationship to ensure the formation of ferroelectric phase. After that, I will move to the PLE growth of epitaxial thin films of $SnTiO_3$ on various single-crystal substrates ($SrTiO_3$, $NdGaO_3$, $DyScO_3$, etc.) to understand the effect of strain on the local and global ferro/piezo responses. In addition, I will grow single crystal $SnTiO_3$ directly on silicon (Si) substrates—the integration of ferroelectrics on Si will be crucial for ferroelectric-based nanoelectronic applications [9–11].

Motivated by previous examples of epitaxial engineering [12,13], I will further synthesize the $ATiO_3/SnTiO_3$ (where A→ Ca and Sr) superlattices (SLs) to study the role of interfacial strain to enhance the spontaneous polarization. These SLs will be fabricating with atomic-scale control by PLE on conducting strontium ruthenate ($SrRuO_3$) layered $SrTiO_3$. The strain in $SnTiO_3$ layers will maintain by controlling the thickness of ferroelectric $SnTiO_3$ layer compare to the non-ferroelectric $ATiO_3$ layers. With strain engineering, an enhancement of the polarization can be expected in these SLs. These studies will develop a new ferroelectric material with enhanced polarization required for dielectric, piezoelectric, and ferroelectric applications. For this project, the main characterization techniques to understand the structure-property relationship will include, X-ray imaging and nano-diffraction, high-resolution scanning transmission electron microscopy, and dielectric and ferroelectric measurements. In addition, scanning probe microscopy (SPM) and its various modes such as, piezoresponse force microscopy (PFM), Kelvin probe force microscopy (KPFM), and conducting atomic force microscopy (CAFM) will be extensively utilizing for nanoscale visualization of ferroelectric domains and/or to study locally modulated functional phenomena. *Based on my research interest to investigating local functionalities using SPM, I intend to develop the various modes of SPM (like, Kelvin probe force microscopy and charge-gradient microscopy) at TTU as they will impact many collaborative efforts.*

P 3: Functional Oxides for Electronic Applications— Complex oxide are very promising materials for advanced electronic applications due to a rich variety of emergent behaviors, such as multiferroics, high-k dielectrics, magnetoelectric, and memristive effects. In this project, the focus will be to utilize the oxide materials for microwave and electro-optic devices (high-entropy perovskite oxides as relaxor ferroelectric and/or dielectrics), magnetoelectric and spintronic devices (high-entropy spinel oxides with tunable magnetic properties and nanodomains), and memristor and synaptic device applications (tin titanates and other polar oxides' capacitors, **Figure 4**). I will explore the possibilities to integrate high quality single-crystal thin films of HEOs with semiconducting substrates. This HEO/semiconductor epitaxy will provide practical relevance to novel ferroic heterostructures and should create funding opportunities with industry.

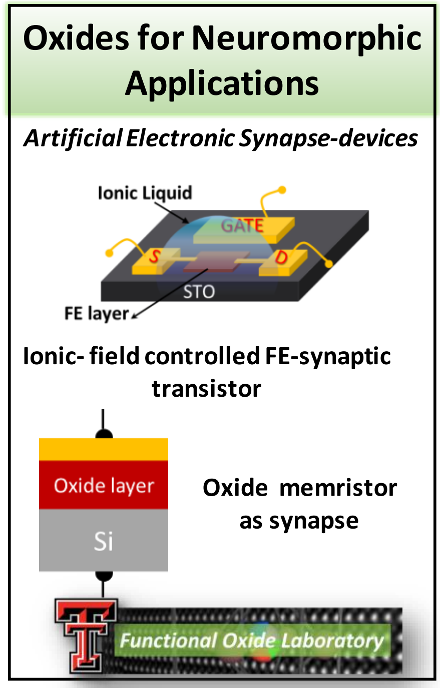

Figure 4. Complex oxide thin films and nanostructures for advanced electronic applications.

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