Sample CNMS User Proposal

Illustrative example | General User Proposal

This example is adapted from a historical CNMS research proposal. Participant identities and administrative records have been replaced or omitted. Scientific descriptions, requested resources, and preliminary-results figures are retained as an illustration of proposal content. It is not a current submission form or a guarantee of award.

General Information

Research title	**Probing the Role of Disorder in Strongly Correlated Single-Crystal High-Entropy Oxide Films**
Proposal type	General User
Principal investigator	Dr. Alex Morgan — Example State University
Collaborators	Dr. Taylor Reed — Sample Research Institute; Dr. Jordan Lee — Illustrative University; Dr. Casey Brooks — Example Materials Laboratory
Planned on-site participation	Dr. Morgan and Dr. Lee: yes; Dr. Reed and Dr. Brooks: remote collaboration
CNMS staff consulted	Relevant scientific staff and capability leads (names omitted)
Research areas	Materials science; condensed matter physics; materials engineering
Samples	Single-crystal perovskite high-entropy oxide films with varied Sr doping and substrate strain
Safety information	No major safety issues identified in the original proposal; all hazards must be reviewed for an actual submission

Participants

Name	Institution	Role	On-site
Dr. Alex Morgan	Example State University	Principal Investigator	Yes
Dr. Taylor Reed	Sample Research Institute	Collaborator	No
Dr. Jordan Lee	Illustrative University	Collaborator	Yes
Dr. Casey Brooks	Example Materials Laboratory	Collaborator	No

CNMS Facilities Requested

Capability	Requested time
Physical Property Measurement System (PPMS)	5 days
Advanced scanning probe microscopy	5 days
AFM/FIB–ToF-SIMS	5 days

Ultrahigh-vacuum STM/STS	10 days
TEM specimen preparation	5 days
Nion UltraSTEM STEM/EELS	3 days
JEOL NEOARM TEM/STEM	3 days
Helium-ion milling and imaging	3 days
Advanced SEM/EDS	4 days

Other Facilities

Additional facility requested: Quantum Design MPMS.

Samples and Identification of Hazards

Sample origin: Wholly supplied by the user; characterized at CNMS.

Materials: Single-crystal ABO3 perovskite high-entropy oxide (La1−xSrx)(Cr0.2Mn0.2Fe0.2Co0.2Ni0.2)O3 films (x = 0, 0.3, 0.5), grown on LaAlO3, LSAT, SrTiO3, and Nb-doped SrTiO3 substrates.

Indicated hazards: No major safety issues identified in the historical proposal. Actual submissions require a complete, current hazards declaration.

Categorization

Materials Sciences (including condensed matter physics and materials chemistry); Engineering.

Funding

Source of support: DOE, Basic Energy Sciences (historical example).

Funding status: Funding obtained.

Review Suggestions

Reviewer keywords: High-entropy oxides; quantum materials; single-crystal films; complex electron coupling.

Description of Proposed Research

1. What is/are the main scientific or technological question(s) that you plan to address?

3d transition metal oxides of the ABO3 perovskite form are important to a range of fundamental and applied interests. Modification of the A and B sites through substitutional doping allows for a wide variety of octahedral distortions and charge states to be tuned. In strongly correlated systems, these shifts to local environment are often central to the emergence of important macroscopic functionalities. We have recently developed entropy assisted synthesis approaches that allow the stabilization of single crystal ABO3 perovskite films possessing 6 or more cations[1-3]. These systems maintain lattice site positional symmetries while permitting the breaking of compositional symmetries. Thus, crystalline materials with a large number of

chaotically placed cations on an oxygen mediated sublattice can create correlated systems where spin, charge, and magnetic exchange interactions are disordered at the local scale. Unexpectedly, these local disorders can paradoxically lead to the emergence of macroscopic charge and magnetic ordering[4] and unexpected macroscopic structural uniformity[5]. How this happens is not understood. Our initial work on element specific magnetic and charge states of the cations in La (Cr0.2Mn0.2Fe0.2Co0.2Ni0.2)O3 films combined with XRD, neutron diffraction, x-ray absorption spectroscopy (XAS), and SQUID magnetometry demonstrate the presence of unexpected and highly tunable magnetic states (see Supplemental Information). The most important result has been that long-range magnetic ordering arises in these materials which are configurationally disordered on all length scales[4]. That is to say that spin state ordering is present in an effectively infinite unit cell where a spin state at any site of square lattice may be influenced by randomly distributed ferromagnetic and antiferromagnetic nearest neighbor exchange coupling. The work outlined in this user proposal is centered around gaining a deeper understanding of the impact of local structural distortions and charge doping on the formation of emergent macroscopic properties. We have synthesized a range of single crystal (La1-x Srx) (Cr0.2Mn0.2Fe0.2Co0.2Ni0.2) O3 (x=0, 0.3, 0.5)(LS5B) films under different strain states (see supporting information). Our preliminary studies show that strain has a strong impact on magnetic properties and that charge doping can be used to modify electronic properties. For example, while X-ray spectroscopy indicates a range of charge states on the cation sites indicating strong electronic disorder, magnetic measurements indicate the presence of long-range magnetic order; for this to happen, there must be some balancing of local spin/charge/lattice(orbital) states to enable this. The ability to populate multiple elements onto a single sublattice in complex crystal structures opens new possibilities to design functionality in correlated systems and enable novel fundamental studies seeking to understand how diverse local bonding environments can work to generate macroscopic responses, such as those driven by electron-phonon channels and complex exchange interaction pathways. For us to begin to understand the mechanisms at play in these new materials, we must understand the local environment around each cation site. This is the central question of this proposal.

2. Outline the overall technical approach that you plan to use to address the above questions. This section should provide the context for research tasks described below in sections (3), home institution activities, and (4), CNMS research.

Our technical approach focuses on imaging across multiple lengthscales in high entropy oxides to understand how compositional disorder(on a positionally ordered lattice) influences dynamics in electronic and magnetic states[prior work, 2021]. We will use strain control in conjunction with hole doping to help disentangle the individual roles orbital and charge parameters play. Importantly, the study of crystalline high entropy oxides is still in its infancy with only a handful of example in literature; for this reason, all information gained in these systems will be novel and important to this growing community. Initial studies have shown an extraordinary degree of magnetic frustration is hosted in La(Cr0.2 Mn0.2 Fe0.2 Co0.2 Ni0.2)O3 single crystal films [4]. To understand this, we need information on element specific distributions and dimensionally resolved charge states to explain how magnetic order and dynamics can emerge from such extreme levels of B-site sublattice disorder. There is little to no data in literature on the fundamental element-specific properties of these materials nor the types of local crystalline distortions present in their structures. We have grown high quality epitaxial LS5B(x=0, 0.3, 0.5) single crystal thin films on LaAlO3 (LAO), (LaAlO3)0.3(SrAl0.5Ta0.5O3)0.7 (LSAT), and SrTiO3 (STO)(and Nb-doped STO for STM experiments) using pulsed laser deposition (Supplemental). XAS shows a complex charge evolution with hole doping that is not evenly spread through between all species on the B-sites while RIXS demonstrates that the Cr edge hosts unexpected delocalized electrons in microscopically insulating crystals. Our central aim is to begin to understand the role of extreme

local disorder on the emergence of macroscopic properties in strongly correlated systems. We are trying to pin down what may be new physical mechanisms lurking in these "perfectly" disordered systems.

3. What research tasks will be carried out at the users' home institution or elsewhere outside of the CNMS? Include any preliminary syntheses, measurements, or tests that have been/will be performed in preparation for the proposed research at the CNMS.

Single crystal thin films of epitaxial [La1-x Srx][Cr0.2 Mn0.2 Fe0.2 Co0.2 Ni0.2]O3 (x=0, 0.3, 0.5) on LaAlO3 (compressive), (LaAlO3)0.3(SrAl0.5Ta0.5O3)0.7 (near lattice matched), and SrTiO3 (tensile) (and on Nb-doped SrTiO3 for STM measurements) will be grown at our home institution. We have conducted x-ray diffraction, atomic force microscopy, several x-ray spectroscopy studies--XAS and RIXS, transport, and DC SQUID magnetometry. Initial characterizations taken on the x=0 sample composition are demonstrated in supplemental. Critical to the proposed work is imaging element specific local cation environments. Gaining a deep fundamental understanding of these materials requires this information. Many of the requested instruments will be used to gain information on composition across a full range of length scales--from pm to mm. This will tie together our interpretation of x-ray spectroscopy observations by allowing us to visualize nearest neighbors and local distortion fields which may be driving the range of observed cation charge states and help theoretically model how macroscopic ordering emerges from local disorder. Page 5 of 10

4. Describe very clearly and specifically the research tasks to be carried out at the CNMS and the expected outcomes from the CNMS tasks. Include any technical milestones that must be met and the need for specialized capabilities and/or expertise at the CNMS for the research to be successful.

1. STM: Temperature dependent dI-dV mapping will be carried out on the x=0 and x=0.5 compositions. Delocalized electrons have been observed in macroscopically insulating x=0.5 films in our RIX experiments(see supplemental). Our intention is to find the inherent lengthscale of the delocalized electrons with atomically resolved mapping of electronic character. This is type of measurement is notoriously difficult in oxides; however we the project team have worked together in the past and accomplished this on a similar (La,Ca)MnO3 composition and feel confident it can be done in these systems[6] using the in-situ annealing loadlock attached to the STM at CNMS. Understanding these delocalization lengthscales will help us interpret unusual magnetic frustration and correlated phase transitions found in these complex systems.

2. TOF-SIMS: will be used on a range of samples to give cross-sectional compositional information. The TOF-SIMS will allow us to check several samples under different strain states at larger length scales. Strain during growth can change stoichiometry near the interface, which is why we need to look at several samples.This will be an important compliment to microscopy work as it will allow us to cover a full range of lengthscales.

3. PLD/RF sputter chamber: will be used to apply thin magnetic permalloy films to compressive, matched, and tensile strained films to look at exchange coupling effects driven by different magnetocrystalline anisotropy. Hall measurements will be conducted on these heterostructures with an eye any anomalous responses.

4. Scanning probes: c-AFM and/or MIM is requested though not critical to the overall success of the project. These techniques would allow us to map mesoscopic insulating-conducting phase coexistence if needed.

5. QD-MPMS: AC susceptibility measurements will be conducted near near magnetic ordering transition temperatures to understand if/how the observed delocalized electronic states impact magnetic frustration and degeneracy. As an example, frustration at the boundary between delocalized and localized electronic states may impose a degree of degeneracy that presents as a glassy behavior.

6. SEM with EDS: will provide gross surface structure and stoichiometry prior to more involved tasks such as TOF-SIMS and STEM sample prep (this is not critical but would likely be helpful).

7.TEM specimen prep: We request access to CNMS sample preparation facilities for preparing TEM samples from thin films. The films would be made through a combination of mechanical polishing/ion milling and Focused Ion Beam milling. We request 5 days each of access for mechanical polishing and FIB sample preparation.

8. JEOL NEOARM: To understand the role of local structure on properties, we need atomic resolution spectroscopy on Sr doped and undoped samples. The first part of the analysis will be performed on the JEOL NeoARM since it is an aberration corrected cold FEG microscope with the capability to perform both atomic resolution EELS and EDX. We would require 3 days of access on the JEOL NeoARM for observing 3 samples (1 per day). We will be looking at the x=0.5 samples on the NeoARM – one compressively strained, one near lattice matched and the third tensile strained. Milestones: High resolution EDX and EELS maps to distinguish La and Sr distribution along with B site dopant distribution. This will be combined with atomic resolution imaging to quantify strain and polar displacements in the film as a function of the distance from the interface, and correlate that to the observed composition obtained from spectroscopic (EELs/EDX) measurements.

9. Nion UltraSTEM: This tool will provide atomic resolution ADF-STEM imaging and EELS mapping to elucidate the local compositional variations in the as grown thin films. We plan on observing 6 samples on the NION. These will be Sr=0 and Sr=0.5 dopings – with each composition having three strain states (compressive, almost zero, tensile). Since multiple samples can be loaded into the NION U100, we would also require 3 days of access to the NION U100, with the goal being the analysis of 2 samples in a single session. Milestones: We will be performing atomic resolution ADF-STEM imaging and core-loss EELS to observe the compositional variation, to check whether they are uniform, and try to understand the relation between lattice strain in the films and chemical compositional variance.

5. Provide an overall timeline for the CNMS tasks and describe how each selected facility, instrument, or computational resource will be used. Include estimates of the number/quantity of samples, instrument time, CPU and/or GPU node hours, or other relevant resource requirements. If computational resources are requested, provide a brief justification describing the types and approximate number of calculations or simulations to be performed and their typical computational requirements (e.g., node counts and runtime).

TOF-SIMS, 6 samples: 5 days JEOL NEOARM, 6 samples: 3 days Nion UltraSTEM, 6 samples: 3 days TEM specimen preparation, 6 samples: 5 days each mechanical and FIB PLD/RF sputter system: 4 days STM, 2 samples: 10 days SEM with EDS, 9 samples: 4 days Scanning probes c-AFM or MIM, 6 samples: 4-6 days MPMS, 3 samples: 5 days

6. What is your team's specific experience and expertise relevant to this research project?

We are one of 3 groups in the world that has demonstrated the ability to synthesize single crystal high entropy oxides. We have extensive experience in the synthesis and characterization of strongly correlated oxide materials. We are familiar with and have worked with CNMS staff on all requested equipment in the past.

Literature Cited

- Single-crystal high entropy perovskite oxide epitaxial films — Physical Review Materials (2018)
- Applying Configurational Complexity to the 2D Ruddlesden–Popper Crystal Structure — ACS Nano (2020)
- Magnetic Texture in Insulating Single Crystal High Entropy Oxide Spinel Films — ACS Applied Materials & Interfaces (2021)

- Designer Magnetism in High Entropy Oxides — arXiv (2021)
- Unexpected crystalline homogeneity from the disordered bond network in high-entropy oxide films — Physical Review Materials (2020)
- Tunable Metallicity of a Manganite Surface by an Oxygen Overlayer — Physical Review Letters (2009)

Note: Author names are omitted from this illustrative bibliography for consistency with the anonymized presentation. Consult the original publications for complete citations.

Preliminary Results

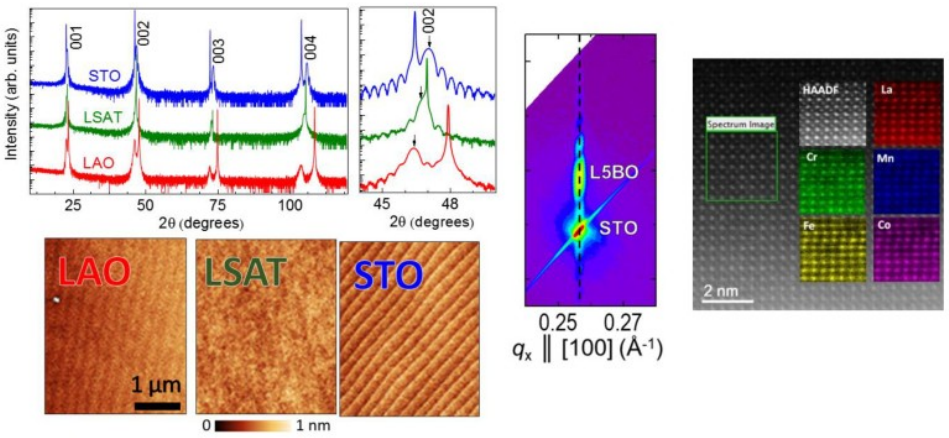


Fig. 1. Example of film quality for La($Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}$)$O_3$ grown on different substrates. (Top Left) XRD. (Botttom Left) AFM surface characterization--Note that films grown on STO have clean unit cell height step terraces where annealing should allow surface termination recovery even after transfer in air to CNMS's STM. (Center) RSM shows uniform epitaxial lock on STO. (Right) Initial STEM-EELS shows uniform mixing of 3d transition metal elements along B-site columns. Synthesis and characterization details can be found at Physical Review Materials **4**, 014404 (2020).

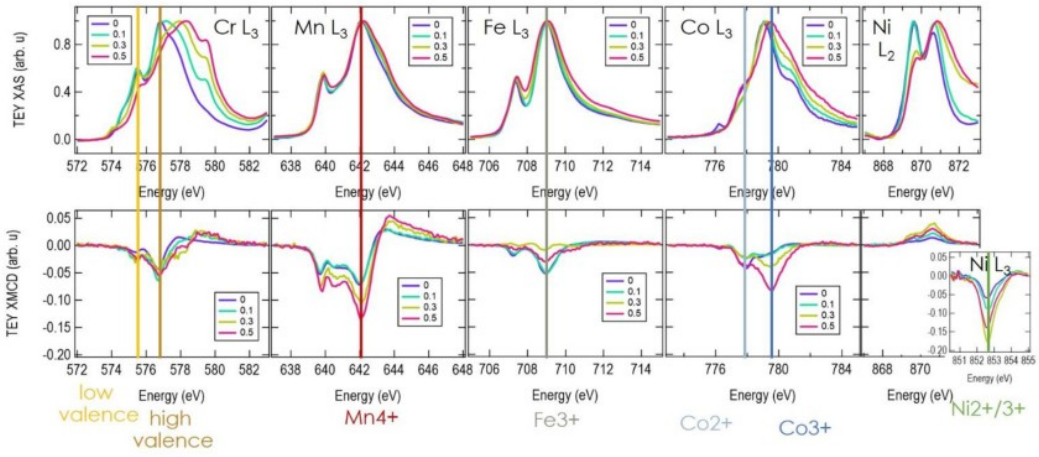


Fig. 2: Initial XAS and XMCD results from [La1-x Srx][Cr0.2 Mn0.2 Fe0.2 Co0.2 Ni0.2]O3 (x=0, 0.1, 0.3, 0.5) films show a disproportionate shift in some elements' charge states as a function of Sr with corresponding shifts in element-specific magnetism.

Figure 1–2. Film quality, structure, surface morphology, and XAS/XMCD results.

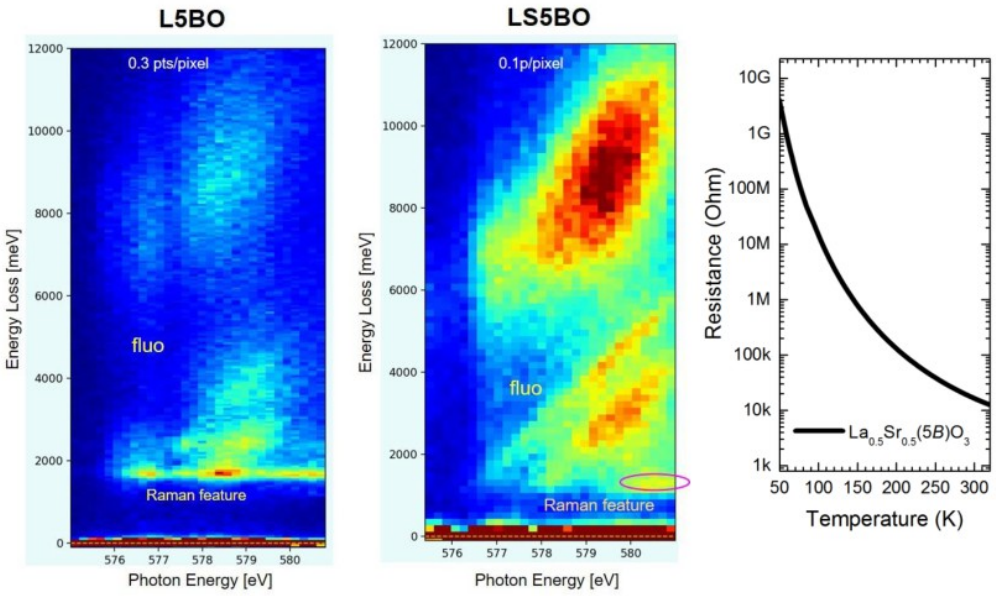


Fig. 3: Initial RIXS energy map of the Cr edge for both the 0% (L5BO) and 50% (LS5BO) films showing a dramatic delocalization of electron character in the 50% doping. Important to note is that both films are macroscopically insulating—example of LS5BO given to right.

Figure 3. RIXS maps and temperature-dependent resistance.