



AFRL-AFOSR-VA-TR-2019-0089

Carrier Doping and Dynamics in Correlated Oxides

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04/11/2019
Final Report

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REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 11-04-2019		2. REPORT TYPE Final Performance			3. DATES COVERED (From - To) 01 May 2016 to 30 Apr 2019	
4. TITLE AND SUBTITLE Carrier Doping and Dynamics in Correlated Oxides				5a. CONTRACT NUMBER		
				5b. GRANT NUMBER FA9550-16-1-0159		
				5c. PROGRAM ELEMENT NUMBER 61102F		
6. AUTHOR(S) Shriram Ramanathan				5d. PROJECT NUMBER		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) PURDUE UNIVERSITY 401 SOUTH GRANT ST WEST LAFAYETTE, IN 47907-2024 US				8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR RTA1		
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-VA-TR-2019-0089		
12. DISTRIBUTION/AVAILABILITY STATEMENT A DISTRIBUTION UNLIMITED: PB Public Release						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT The overarching goals of the project include fundamental studies of carrier doping mechanisms of correlated oxides and insitu measurements at a synchrotron beamline. Recently, we have designed a new approach to dope correlated oxides using biological interfaces. This methods allows electron doping that is confined to near-surface regions with no need for external energy input. This is accomplished by enzymatic anchoring to electrodes placed on the correlated oxide surface. This mechanism has been studied in detail using angle dependent NEXAFS to show that the doping is confined to the top few nms. Collaborative studies on the doping using different enzymes have allowed us to establish the general principles for near-surface doping of correlated nickelates.						
15. SUBJECT TERMS correlated oxide, NbO₂, EuNiO₃, neutron scattering, X-ray scattering, transport						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON GORETTA, KENNETH	
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 703-696-7349	

Project title: Carrier doping and dynamics in correlated oxides
AFOSR Award: FA9550-16-1-0159
PI: Shriram Ramanathan, Purdue University

Progress Report

Scientific background

The electronic properties of functional oxide perovskites are related to microstructure, local bonding and orbital occupancy. SmNiO_3 (SNO) is a prototypical rare-earth nickelate, having a formula of (ABO_3) . Charge disproportionation at the Ni site was proposed as the origin for metal-insulator (MIT) phenomenon. The small band gap of SNO sets the limitation for magnitude of the resistance change through phase transition is therefore only about 1-2 orders. Electron doping, however, has been experimentally demonstrated to achieve colossal resistance changes. With one extra electron injection into Ni e_g orbital, $\text{Ni}^{3+} t_{2g}^6 e_g^1$ is converted into $\text{Ni}^{2+} t_{2g}^6 e_g^2$ with a high spin configuration because of coulomb repulsion in the octahedral field formed by neighboring oxygen ligands. Compared to the very small band gap (a few hundred meV) induced by charge disproportionation in SNO, the strong Hubbard Coulomb interaction U existing in high spin e_g^2 orbitals of Ni^{2+} will generate a much larger band gap (several eV). This will cause a colossal resistance (up to 8-10 orders) increase in the electron doped SNO. Fundamental research to understand the mechanisms and dynamics are therefore necessary to understand the origins of this electronic transition.

Summary: We have advanced a new approach to realize colossal insulator-metal transitions in perovskite nickelates by electron doping from donors such as hydrogen or lithium that is not temperature dependent. This transition is distinct from thermally-driven transitions previously noted in nickelates as well as other correlated oxides. Nickelates such as SmNiO_3 can be transformed into strongly correlated insulators by orbital-specific electron doping. When dopants such as hydrogen or lithium are inserted into the nickelate lattice from ion reservoirs, the dopant splits into a proton/lithium ion and electron. The proton is located in an interstitial site while the electron is anchored into the Ni e_g orbitals. At doping level approaching one electron per unit cell, the emergent electron localization is accompanied with electrical resistivity change of $\sim 10^{10}$ orders of magnitude and 3 eV optical gap change at ambient conditions. The mechanism of this doping-driven phase change has recently been shown to be control of Ni orbital occupancy evolving from $t_{2g}^6 e_g^1$ to $t_{2g}^6 e_g^2$ for each added electron from X-ray absorption spectroscopy. Neutron reflectometry proved the dopant incorporation into the lattice by deuterium isotope experiments.

Principal Results

Synchrotron X-ray spectroscopic studies of SmNiO_3 doped from aqueous solutions

In-situ synchrotron X-ray reflectivity (XRR) (Figure. 1(a)) was performed on SNO submerged in 0.01M KOH water solution to investigate the microscopic mechanism of change in resistance. Synchrotron X-ray measurements of the SNO samples were carried out on a five-circle diffractometer with χ -circle geometry, using an X-ray energy of 20 keV (wavelength $\lambda = 0.6197$ Å) at sector 12-ID-D of the Advanced Photon Source, Argonne National Laboratory. The X-ray beam at the beamline 12ID-D has a total flux of 4.0×10^{12} photons/s and was vertically focused by beryllium compound refractive lenses to a beam profile below 50 μm . The Q_z -scan or L-scan

was obtained by subtracting the diffuse background contributions using the two-dimensional images acquired with a pixel 2D array area detector (Dectris PILATUS-1mm Si 100K).

For *in-situ* XRR, epitaxial SNO samples with thickness of 70 nm were grown on LaAlO_3 (001) substrate. The sample was attached to an *in-situ* electrochemical cell (Figure. 1(a)) filled with the 0.01 M KOH aqueous solution. The XRR data of SNO was measured *in-situ* after applying bias potential of -1.5 V (vs. Ag/AgCl) for 3 min and 9 min. Upon applying bias potential of -1.5 V [Figure. 1(b)], the XRR shows a noticeable decrease in the oscillation period with increasing the duration of applied potential [Figure. 1(b) inset], indicating a significant expansion of film thickness. X-ray diffraction measurements over wide range were carried out using the PANalytical MRD X'Pert Pro with $\text{Cu } K_\alpha$ X-ray (wavelength $\lambda = 1.5418 \text{ \AA}$). The measurements were carried out on SNO samples after being treated in 0.01 M KOH at -4.0 V (vs. Ag/AgCl) for 5 min. It is seen from Figure 1(c) that no new peaks appear after the water-treatment which is distinct from the significant lattice reconstruction that has been noted in other oxides such as cobaltites upon exposure to water. Synchrotron X-ray diffraction curves obtained near the (220) peak of SNO in pristine and water-treated state are shown in Figure. 1(d). The (220) peak of pristine SNO (orthorhombic notation) appears at $Q_1 \sim 3.29 \text{ \AA}^{-1}$ as a shoulder with slightly lower Q_z than LaAlO_3 (LAO) (002) diffraction peak (pseudocubic notation), demonstrating the epitaxial growth of SNO on LAO. After the water-treatment, the epitaxial relationship of SNO on LAO is preserved. Peak 1 shifts to lower Q_z . Peak 2 appears at $Q_z = 3.11 \text{ \AA}^{-1}$, which corresponds to increase of lattice constant by $\sim 5.7\%$.

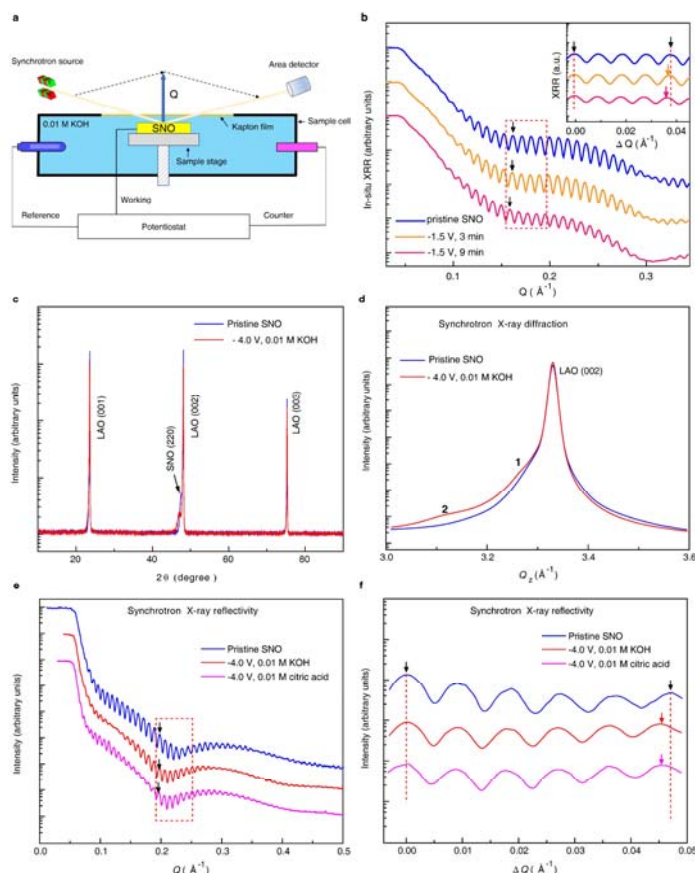


Figure 1. X-ray reflectivity and X-ray diffraction of water-treated SNO. (a) A schematic of the experimental setup for *in-situ* XRR measurement at the Advanced Photon Source. (b) Comparison of *in-situ* synchrotron X-ray

reflectivity (XRR) curves for pristine and water-treated SNO thin film after applying bias for 3 and 9 min successively. Inset shows enlarged area of the XRR curves normalized to the oscillation peak at $Q \sim 0.16 \text{ \AA}^{-1}$. (c) XRD profiles of SNO and water-treated SNO over wide 2θ range. (d) Synchrotron X-ray diffraction curves taken from SNO/LAO thin film after treatment in 0.01 M KOH aqueous solution at -4.0 V for 30 s. (e) Comparison of synchrotron X-ray reflectivity (XRR) curves for SNO after applying bias of -4.0 V and 5 min in 0.01 M citric acid and 0.01 M KOH respectively. (f) The selected area of the XRR curves normalized to the oscillation peak at $Q \sim 0.19 \text{ \AA}^{-1}$ [marked by black arrows in (e)]. Upon treatment, the XRR oscillation period decreases demonstrating the film expansion regardless of solution type, indicating a general mechanism of phase change of SNO in various aqueous solutions due to proton incorporation.

Additional *ex-situ* XRR measurements of SNO in various aqueous solutions were carried out. The samples were treated separately in 0.01 M citric acid and 0.01 M KOH aqueous solutions by applying same bias potential of -4.0 V (vs. Ag/AgCl) for 5 min. Synchrotron X-ray investigations (Figure. 1(e) and 1(f)) show that such a film expansion which is indicated by decrease of oscillation period occurs regardless of solution.

A. Neutron reflectivity measurements and deuterium isotope exchange studies

Neutron scattering is uniquely sensitive to hydrogen and further can distinguish isotopes. This is among the most suited techniques to investigate proton dynamics in solids due to the extreme experimental challenge of light element detection in a solid matrix. The neutron reflectometry (NR) measurements were performed at NIST Center for Neutron Research using the MAGIK reflectometer. The samples were characterized in the neutron beam over the Q range 0-0.18 $\text{\AA}^{-1}$. The NR data fittings were performed with NIST Refl1d software package. For NR isotope substitution measurement, the SNO sample with thickness of ~ 70 nm was grown on Si (100) substrate. The sample was cleaved into two pieces. One piece of SNO was characterized first at pristine state as a reference. This sample was then treated at -4.0 V (vs. Ag/AgCl) for 30 s in 0.01 M KOH/H₂O solution. To observe contrast from isotope substitution, the other piece of SNO was treated at -4.0 V (vs. Ag/AgCl) for 30 s in 0.01 M KOH/D₂O solution. After the treatment, samples were cleaned in isopropanol and dried in ambient conditions before measurements.

Neutron reflectivity (NR) curves of SNO are shown in Figure. 2(a) for the pristine film as well as after treatment in D₂O (heavy water) and H₂O solutions respectively. The decrease in oscillation period in the NR results after either H₂O or D₂O treatment [Figure. 2(a) inset] corresponds to $\sim 6.9\%$ film expansion and decrease of film density from $5.4 \times 10^{-6} \text{ \AA}^{-2}$ in pristine SNO to $4.6 \times 10^{-6} \text{ \AA}^{-2}$ in deuterated SNO and $4.1 \times 10^{-6} \text{ \AA}^{-2}$ in hydrogenated SNO. The surface roughness is nearly unchanged after water treatment (~ 0.7 nm in both pristine and deuterated SNO), indicating the integrity of samples.

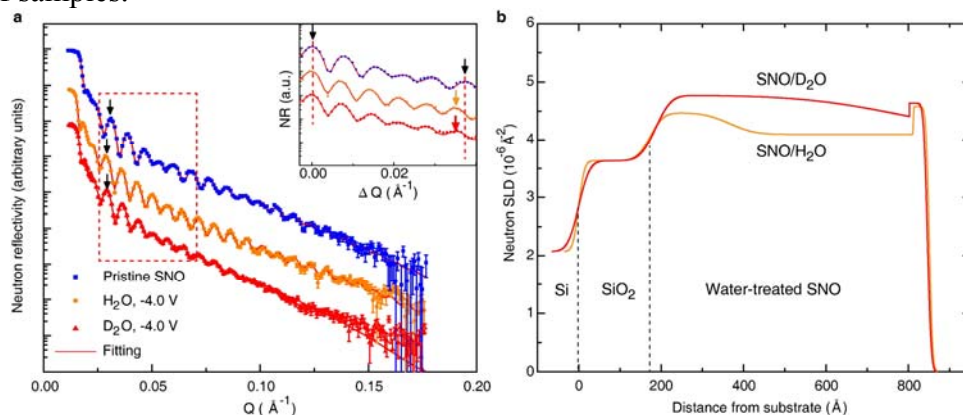


Figure 2. Neutron reflectivity measurements of water-treated SNO. (a) Neutron reflectometry data, error bars, and associated fits comparing pristine, hydrogenated, and deuterated SNO thin films. Error bars and uncertainties represent one standard error. Inset shows an enlarged area comparing oscillations normalized to the peak at $Q \sim 0.03 \text{ \AA}^{-1}$. (b) The SLD profiles were fitted to data shown in (a) for the SNO/SiO₂/Si films. The profiles of water-treated and heavy-water-treated samples show similar film expansion. However, a contrast between the SLD of D₂O and H₂O treated films appears. Since the D⁺ possesses larger neutron scattering length than H⁺, the increase of SLD demonstrates the intercalation of D⁺ from the D₂O into the lattice after the treatment.

The fitted neutron scattering length density (SLD) profiles (Figure. 2(b)) show significant increase in the SNO region when H₂O is replaced with D₂O. It is consistent with the larger neutron scattering cross section of D⁺ relative to H⁺. The isotopic substitution results therefore show clearly the intercalation and transport of H⁺ (or D⁺) from the solution to SNO during the water-treatment.

Extended X-ray absorption fine structure (EXAFS) analysis of Li-doped SmNiO₃

To further demonstrate the interstitial doping mechanism, we carried out EXAFS analysis on representative nickelate films doped with lithium ions.

1 M of LiClO₄ (Sigma Aldrich) was dissolved in polyethylene carbonate (PC) in an argon filled glovebox with oxygen and moisture levels at < 0.5 ppm. A drop of 1M LiClO₄ | PC was dispersed on SNO | LAO thin film. A commercial LiCoO₂ supported on current collector Al foil was used as lithium source for lithiation. As separator, a piece of Polymer membrane (Celgard 2500) is placed underneath the LiCoO₂ | Al foil avoiding the direct contact to SNO | LAO thin film as shown in Figure 3. A positive bias is applied to the LiCoO₂ | Al foil and thin film serves as the ground electrode for lithiation process. By varying the time over the range of few seconds to couple of hours, we can spatially vary the extent of doping and consequently the charge localization through the film thickness.

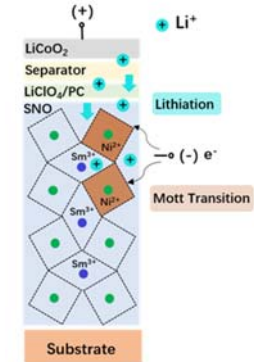
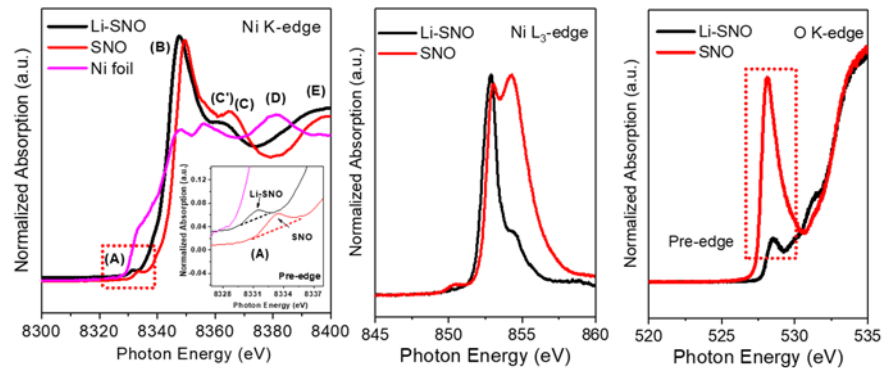


Figure 3: Schematic of experimental setup to dope SmNiO₃ with lithium

The Ni K-edge X-ray spectra (XAS) were performed using linear polarized X-rays at the undulator beamline 20-ID-C of the Advanced Photon Source (APS), Argonne National Laboratory. Ni L_{2,3}-edge and O K-edge X-ray absorption spectra (XAS) were collected by using both total electron yield (TEY) through drain current measurements and partial fluorescence yield (PFY) modes at the CSX-2 (23-ID-2) beamline of National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory. PFY spectra were collected using a Vortex silicon drift detector.



We characterized the films with X-ray absorption near edge spectroscopy (XANES)

to probe the electronic structure evolution. In the normalized Ni K-edge XANES (Figure 4a), the pre-edge (feature A) points to the covalence between O_{2p} and Ni_{3d} orbital. The rest of absorption features essentially stem from two different coordination shells, e.g., the first shell (in feature B,D,E) is formed by octahedral oxygen coordination while the second shell (feature C and C') is due to rare-earth atoms in a pseudocubic coordination. (144) The intensity of feature A (inset of Figure 4a) significantly decreased after lithiation, indicating the Ni valence decrease. Ni L_{3} -edge spectra of SNO also shows drastic changes after lithiation with diminished peak at ~ 855 eV, stressing the transition of Ni^{3+} to Ni^{2+} (Figure 4b). A detailed comparison of pre-edge area (Ni K-edge) clearly shows that the lithiation process decreases the concentration of ligand hole ($3d^8\bar{L}$ in the ground state of Ni, where L denotes a hole state generated in ligand p orbital) by 40%. Further study on the O K-edge spectra (Figure 4c) indicates a reduced O-projected density of unoccupied states due to lithiation induced electron filling, suggesting the formation of Ni^{2+} .

The rest of the holes within O^{2-} could bond with Li^+ and facilitate its transport. The first derivative plot of the Ni K-edge XANES presents a shift of the pre-edge and absorption edge toward lower energy by 1.65 eV for the 2 hour-lithiated sample. An effective change in valence of -1 for the Ni ions is seen here.

The first derivative plot of the Ni K-edge XANES spectra (Figure 5) shows that the energy separation between A and B feature is ~ 16.45 eV for pristine SNO which is larger than that of Li-SNO (~ 15.35 eV). The significant change in energy splitting suggests that lithiation enhances the lattice distortion and increases the Ni-O bond length.

The fitted Fourier transformed extended X-ray absorption fine structure (EXAFS) spectra (Figure 6) gives a local picture of the Ni coordination shells. For pristine SNO, the Fourier Transfer amplitude near $1.5 \text{ \AA}$ corresponds to the Ni-O bond, while the Fourier Transfer amplitude near $2.6 \text{ \AA}$ corresponds to the Ni-Sm bond. After lithiation, the intensity of the Ni-O feature is weakened with a clear shift. The coordination number decreases from 5.56 to 4.52, quantitatively indicating an increase in structural disorder. Meanwhile, a distinct Fourier transfer amplitude appears near $2.2 \text{ \AA}$ on Li-SNO (The dash vertical line in Figure 6), which is located between the Ni-O distance and the Ni-Sm distance. This implies that an additional shell

Figure 4: Electronic and structural configuration of Li-SNO. a, Ex-situ normalized Ni K-edge b, Ni L_{3} -edge c, O K-edge of X-ray absorption near-edge spectroscopy (XANES) characterization of pristine SNO and Li-SNO. As a reference, the spectrum of Ni foil was used for energy calibration.

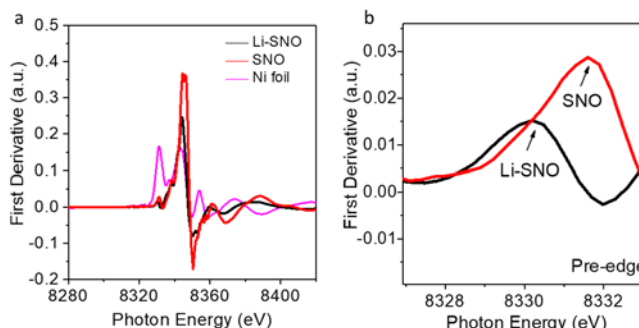


Figure 5. First derivative XANES of Ni K-edge of pristine SNO and Li-SNO. a. First derivative of normalized XANES of SNO and Li-SNO. Nickel metal is used as reference. b.. Zoom in figure of pre-edge of first derivative of the normalized XANES spectra.

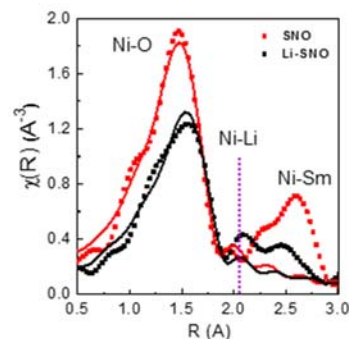


Figure 6. Fourier transform of the Ni K-edge EXAFS (dots) and the fitting (lines) of SNO and Li-SNO.

between the O shell and the Sm shell does exist around the central Ni atom and can originate from interstitially distributed Li dopant atoms (Ni-Li shell).

Archival Publications

- Perovskite nickelates as bio-electronic interfaces, H. T. Zhang et al, *Nature Communications* (in press, 2019)
- Beyond electrostatic modification: design and discovery of functional oxide phases by ionic-electronic doping, H. T. Zhang, Z. Zhang, H. Zhou, H. Tanaka, D. D. Fong and S. Ramanathan, *Advances in Physics X*, Article: 1523686 (2018)
- Strongly correlated perovskite lithium ion shuttles, Y. Sun, M. Kotiuga, D. Lim, B. Narayanan, M. Cherukara, Z. Zhang, Y. Dong, R. Kou, C. J. Sun, Q. Lu, I. Waluyo, A. Hunt, H. Tanaka, A. N. Hattori, S. Gamage, Y. Abate, V. G. Pol, H. Zhou, S. K. R. S. Sankaranarayanan, B. Yildiz, K. M. Rabe, and S. Ramanathan, *Proceedings of the National Academy of Sciences of the USA*, 115, 9672 (2018)
- Quantum materials for brain sciences and artificial intelligence, S. Ramanathan, *MRS Bulletin*, 43, 534 (2018)
- Perovskite nickelates as electric-field sensors in salt water, Z. Zhang, D. Schwanz, B. Narayanan, M. Kotiuga, J. A. Dura, M. Cherukara, H. Zhou, J. W. Freeland, J. Li, R. Sutarto, F. He, C. Wu, J. Zhu, Y. Sun, K. Ramadoss, S. Nonnenmann, N. Yu, R. Comin, K. M. Rabe, S. K. R. S. Sankaranarayanan and S. Ramanathan, *Nature*, 553, 68 (2018)

Invited talks (SR)

- ACerS Electronic Materials and Applications, 2019 (Orlando, FL)
- SPIE DSS conference, 2019 (Baltimore, MD)
- International Workshop on Oxide Electronics, 2019 (Kyoto, Japan)
- Frontiers of Oxide Devices and Materials Symposium, 2018 (Kobe, Japan)
- APS March Meeting, 2018 (Los Angeles)

Significant collaborations

- Collaborated with Dr. J. A. Dura (NIST); Dr. H. Zhou, Dr. J. W. Freeland (ANL) to investigate oxide films by neutron scattering and synchrotron spectroscopy
- Collaborated with Dr. Y. Abate (Georgia) to study THz response to carrier localization nickelates before and after doping
- Collaborated with Dr. K. M. Rabe (Rutgers) to compare first principles calculations to experimental measurements change in resistivity due to electron doping and also strain evolution due to interstitial dopant incorporation

Students graduated

- One student (D. Schwanz) who was supported for part of his PhD duration by the AFOSR grant graduated in 2018.