Abstract

ROST, CHRISTINA MARY. Entropy-Stabilized Oxides: Explorations of a Novel Class of Multicomponent Materials (Under the direction of Professor Jon-Paul Maria).

An ever-present challenge for scientists and engineers is to develop new materials that are innovative enough to set a new technological precedent and maintain application relevance for a substantial timeframe. There are many ways in which materials are exploited for new or improved properties, including but not limited to compositional substitution, doping, strain induction, or synthesis variation. The call for the Materials Genome Initiative has invoked the combined effort between theoreticians, experimentalists and industrialists to explore and apply material systems never before seen. One such strategy for new materials exploration is the development of high entropy alloys (HEAs). In HEAs, the addition of five or more component materials increases configurational entropy such that the resulting system contains fewer phases than traditionally expected, most of which are solid solutions. Research in this field is continuing to find new and exciting properties, with high potential for technological implementation.

This thesis extends the idea of HEAs to oxide materials — that configurational disorder can be compositionally engineered into complex oxide solid solutions. This work narrates a series of exploratory studies intended as gateways to many possible avenues of further research on a new class of materials called Entropy-Stabilized Oxides (ESO). Chapter one summarizes the inspiration for this work and provides some basic background thermodynamics. The difficult task of materials development and some common approaches to such a task are discussed. Chapter two describes the primary experimental methods used in this work and their generalized parameters. Chapter three contains original work published in Nature Communications. This chapter explains a series of rigorous experiments on a five-component oxide formulation, J14 a rocksalt structure containing equal amounts of Mg, Co, Cu, Ni and Zn randomly
distributed among the cation sublattice, and oxygen on the anion sublattice. Here it is demonstrated beyond reasonable doubt that entropy can drive a reversible transformation between a multi-phase and single-phase state. Additional characterization finds the cation distributions of the prototype ESO proven to be random and homogeneous. Chapter four focuses on the measurement and analysis of extended x-ray absorption fine structure of four of the five cation species present in the prototype ESO composition J14. It is found that the local disorder around each absorbing cation becomes averaged into the unit cell structure as soon as the second coordination shell, and maintained that the ESO composition is a solid solution on the smallest possible length scale. Chapter five explores the hypothesis that PLD provides sufficient energy to overcome kinetic and thermodynamic barriers due to temperature limitations of bulk synthesis, making additional ESOs accessible; including, but not limited to, those compositions that do not form a solid solution under normal synthesis conditions up to 1650 °C and compositions with more than five different cation species. Here, three additional compositions—those only stable in thin film form—are presented. Chapter six discusses the finding that systematic thin film growth of an entropy-stabilized host containing a sixth component element results in lattice distortion changes with deposition temperature. Identical growth conditions of the solitary host find a unique change in lattice parameter between 350 °C to 400 °C where the out-of-plane lattice constant shifts discretely from a small value to a large one. Several experiments are undertaken to isolate the cause for this ongoing trend. Specific compositional trends are discussed, substrate effects are negated, pressure effects are explored, and a hypothesis of competition between cation oxidation states is formulated. Chapter seven includes concluding remarks and a few possibilities for future work.
Dedication

To my father…here’s that doctorate you’ve been so eagerly awaiting…
Biography

Christina Mary Rost was born on February 15, 1987 to parents Allen and Cynthia Rost of Speers Hill, Pennsylvania. After graduating Charleroi High School in 2005, Tina enrolled as a double major in Physics and Physics Education with a minor in mathematics at Indiana University of Pennsylvania. During her senior year of undergraduate studies, Tina began research under Dr. Gregory Kenning working on the relaxation time scales of magnetic spin-glasses. Upon graduation in 2009, Tina remained working with Dr. Kenning in pursuit of a M.S. Physics degree where she designed, built and automated a dual DC SQuID magnetometer for relaxation studies. Meanwhile, she also held a graduate assistantship in the department of Liberal Studies, docketing new course proposals for the University-Wide Undergraduate Curriculum Committee. In 2011, she was hired as an adjunct faculty member within the IUP physics department and taught undergraduate physics laboratory sequences to both major and non-major classes. Tina joined the Complex Oxides and Thin Films Group at North Carolina State University in 2012, under the direction of Dr. Jon-Paul Maria, in pursuit of a Ph.D. in Materials Science and Engineering. Her work involved the development of a new class of complex oxide systems, called Entropy-Stabilized Oxides. Since 2013, Tina has established and led a local Wake County Girl Scout troop alongside two other MSE graduate students, Dr. Lindsay Hussey and Miss Jessica Nash.
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Ultimately, I owe tremendous gratitude to my advisor, Dr. Jon-Paul Maria. If it weren’t for his support, uncanny problem-solving abilities, and extreme optimism in the face of impending scientific doom, I wouldn’t be writing this dissertation.

I wish to express my love and appreciation for my family. Glenn, my husband, whose kindness and patience trumps any person I’ve ever known; my parents, Al and Cindy, and my brother, A.J., who continue to support me unconditionally.

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# Table of Contents

List of Tables ......................................................................................................................... xi
List of Figures ......................................................................................................................... xii

1 Introduction .......................................................................................................................... 1
   1.1 Materials and Technology ........................................................................................... 1
   1.2 An Alternative Approach to Materials Development ...................................................... 3
   1.3 Basic Thermodynamic Principles .................................................................................. 7

2 Experimental Methods ........................................................................................................ 14
   2.1 Powder Processing ....................................................................................................... 14
   2.2 Pulsed Laser Deposition ............................................................................................. 15
      2.2.1 Target Preparation ............................................................................................... 15
      2.2.2 PLD-System Setup ............................................................................................. 15
      2.2.3 Thin Film Deposition ......................................................................................... 16
   2.3 Characterization Techniques ......................................................................................... 17
      2.3.1 X-Ray Diffraction (XRD) .................................................................................... 17
      2.3.2 Differential Scanning Calorimetry (DSC) ............................................................. 17
   2.4 X-Ray Absorption Fine Structure (XAFS) .................................................................... 19
      2.4.1 Sample Preparation ............................................................................................. 19
      2.4.2 XAFS Measurements ......................................................................................... 21

3 Entropy-Stabilized Oxides ................................................................................................... 24
   3.1 Abstract ....................................................................................................................... 24
   3.2 Main Text .................................................................................................................... 25
      3.2.1 Results ................................................................................................................ 27
      3.2.2 Discussion .......................................................................................................... 38
      3.2.3 Methods ............................................................................................................. 43
   3.3 Acknowledgements ...................................................................................................... 51
   3.4 Author Contributions ................................................................................................. 51
   3.5 Supplementary Materials ............................................................................................ 52

4 Local Structure of the Mg$_{x}$Ni$_{x}$Co$_{x}$Cu$_{x}$Zn$_{x}$O($x=0.2$) Entropy-Stabilized Oxide: An EXAFS Study .......................................................................................................................... 62
   4.1 Abstract ....................................................................................................................... 62
   4.2 Introduction ................................................................................................................. 63
7 Conclusions and Future Work ...................................................................................... 157
  7.1 Conclusions ........................................................................................................... 157
  7.2 Future Work ........................................................................................................... 159

References .................................................................................................................. 162

Appendix A Compositions ............................................................................................ 175

Appendix B EXAFS ........................................................................................................ 177
  B.1 Theory and Explanation ......................................................................................... 177
  B.2 Data Processing ..................................................................................................... 182
  B.3 Data Fitting Using a Theoretical Standard ........................................................... 194

Appendix C Additional Work ......................................................................................... 203
  C.1 Kissinger Analysis ................................................................................................. 203
  C.2 Linear Thermal Expansion of J14 ........................................................................ 206
  C.3 Neutron Pair Distribution Function Study ............................................................ 207
List of Tables

Table 2.1 Table of EXAFS scattering cross sections, absorption lengths, and calculated mass. .................................................................................................................................................. 20
Table 3.2 List of compositions used to prepare the transition temperature phase diagrams in Figure 3.2(c-g) in the main text................................................................. 53
Table 3.3 Calculated relative intensity ratios for J14. ......................................................... 55
Table 3.4 Elements measured at APS beamline 12-BM-B. ................................................ 55
Table 4.1 EXAFS cross sections, absorption coefficients, and absorption lengths for energy edged pertaining to Co, Ni, Cu and Zn cations. ......................................................... 66
Table 4.2 Results of best fits for Ni, Co, Zn and Cu cations in J14. ......................... 72
Table 5.2 List of components in each composition and their respective molar percentage: T22, J14C, and J30. .................................................................................................................. 94
Table 5.3 Calculation of lattice parameter for T22 rocksalt grown on (100) Si. The calculated standard deviation is ± 0.004. ........................................................................ 97
Table 6.1 List of compositions used in this study. .............................................................. 124
Table A.1 Compositions ...................................................................................................... 175
Table B.1 Definitions of EXAFS equation terms. ............................................................ 181
List of Figures

Figure 1.1 The typical materials development process. .......................................................... 1
Figure 1.2 Variation of thermodynamic mixing properties a) $\Delta H_{\text{mix}}$, b) $\Delta S_{\text{mix}}$, and c) $\Delta G_{\text{mix}}$ as a function of composition and temperature for the simplest regular solution model. Adapted from [49]. .......................................................................................... 10
Figure 1.3 Plot of energy versus temperature, illustrating temperature dependence of enthalpy and Gibbs free energy. Adapted from [62]. ................................................................. 12
Figure 2.1 PLD system setup ................................................................................................. 15
Figure 2.2 DSC sample carrier configuration ..................................................................... 18
Figure 2.3 Photograph of EXAFS sample. Powder is evenly dispersed on Kapton tape, and folded three times to create a 1 cm x 1 cm square. Kapton is x-ray transparent, and the tri-fold creates the correct number of layers corresponding to appropriate sample thickness. ........................................................................................................ 20
Figure 2.4 Transmission setup for EXAFS measurements on beamline 12-BM-B at the Advances Photon Source, Argonne National Laboratories ........................................... 22
Figure 2.5 Example of typical absorption spectra obtained from a XAFS measurement using metal reference foils ........................................................................................................ 23
Figure 3.1 X-ray diffraction patterns for high entropy formulation J14. J14 consists of an equimolar mixture of MgO, NiO, ZnO, CuO, and CoO. The patterns were collected from a single pellet. The pellet was quenched to room temperature by direct extraction from the furnace. X-ray intensity is plotted on a logarithmic scale and arrows indicate peaks associated with non-rocksalt phases, peaks indexed with (T) and with (RS) correspond to tenorite and rocksalt phases respectively. The two x-ray patterns for 1000 °C annealed samples are offset in 2θ for clarity. ......................................................................................................................... 28
Figure 3.2 Compositional analysis. (a) X-ray diffraction analysis for a composition series where individual components are removed from the parent composition J14 and heat-treated to the conditions that would otherwise produce full solid solution. Asterisks identify peaks from rocksalt while carrots identify peaks from other crystal structures. (b) Calculated configurational entropy in a N-component solid solution as a function of Mol% of the Nth component. (c)-(g) Partial phase diagrams showing the transition temperature to single phase as a function of composition (solvus) in the vicinity of the equimolar composition where maximum configurational entropy is expected. Error bars account for uncertainty between temperature intervals. Each phase diagram varies systematically the concentration of one element. .................................................................................. 31
Figure 3.3 Demonstrating endothermicity. (a) in situ x-ray diffraction intensity map as a function of 29 and temperature, and (b) differential scanning calorimetry trace for formulation J14. Note that the conversion to single phase is accompanied by an endotherm. Both experiments were conducted at a heating rate of 5 °C/minute. ... 33
Figure 3.4 Extended x-ray absorption fine structure. EXAFS measured at APS beamline 12-BM after energy normalization and fitting. Note that the oscillations for each element occur with similar relative intensity and at similar reciprocal spacing. This suggests a similar local structural and chemical environment for each. ................................. 35
Figure 3.5 STEM-EDS analysis of J14. (a) is a HAADF image. Panels labeled as Zn, Ni, Cu, Mg and Co are intensity maps for the respective characteristic x-rays. The individual
EDS maps show uniform spatial distributions for each element and are atomically resolved.

Figure 3.6 A binary metal compared to a ternary oxide. A schematic representation of two lattices illustrating how the first near-neighbor environments between species having different electronegativity (the darker the more negative charge localized) for (a) a random binary metal alloy, and (b) a random pseudo-binary mixed oxide. In the latter, near-neighbor cations are interrupted by intermediate common anions.

Figure 3.7 Expanded view of one XRD temperature ladder showing the progression to single phase with 25 °C annealing steps. Red arrows indicate second phases, green and blue arrows indicate shoulders of second phases associated with wurtzitic and rocksalt structures respectively. Dashed lines highlight relative intensity values. Note that for rocksalt, I_{111} cannot be larger than I_{200}, thus we can use the relative intensity values as a co-indicator of the final transition to single phase.

Figure 3.8 DSC and TGA analysis for pure CuO powder collected under the identical conditions as sample J14, 25 °C/minute ramp in flowing air.

Figure 3.9 Relative XAFS spectra as measured at APS beamline 12-BM after background normalization.

Figure 3.10 X-ray analysis in the (left) two-theta and (right) omega circles for a {001} J14 film grown on an MgO single crystal substrate. The rocking curves were collected at the optimized 29 positions for the film and substrate respectively. Both rocking curves have full-width-half-maximum values of 0.017 °.

Figure 3.11 False colored selected area electron diffraction pattern for formulation J14 taken along a <001> direction. There is no evidence of second phases.

Figure 3.12 A lower magnification HAADF STEM image of formulation J14 (left) and a composite STEM EDS map (right). In this map, the colors correspond to characteristic x-ray intensities where blue=Mg, purple=Co, green=Ni, orange=Cu, and red=Zn. Note that the areal distribution of colors is random and free from clustering.

Figure 3.13 Calculated configurational entropy in a N-component solid solution as a function of Mol% of the N^{th} component. The black dots indicate the compositions with maximum configurations and for each N value occur at the equimolar elemental ratios. The same calculation produced the data in Figure 3.2(b).

Figure 4.1 X-ray diffraction (XRD) pattern for reacted and hand milled J14 powder used for EXAFS measurements. Pattern shows a single phase rocksalt structure with both Cu Ka1 and Ka2 peaks present.

Figure 4.2 EXAFS spectra (χ(k)) for a) cobalt b) copper c) nickel and d) zinc within a single J14 powder sample.

Figure 4.3 The Fourier transform of each EXAFS spectra for a) cobalt, b) nickel, c) zinc, and d) copper. It can be observed that the second coordination shell for each absorber appear to be in the same position in R. Ni, Co and Zn have similar nearest neighbor positions while Cu exhibits both a significant shift to lower R, as well as a decrease in peak amplitude.

Figure 4.4 Diagram depicting 2D, 2 x 1 unit cell of J14 rocksalt. The scattering path characteristic of the second nearest neighbors is the equivalent distance of one half the face diagonal in an FCC unit cell. The total magnitude of the face diagonal, 5.982Å, corresponds to a cubic lattice parameter of 4.23Å.
Figure 4.5 R-factor vs. N for Co, Cu, Ni, and Zn cations. The increasing R-factor indicated that as the number of cation species is increased, the fit quality degrades. Based on four of five cations having this trend, it can be assumed to be similar with Mg as well. 

Figure 5.1 Diagram illustrating growth of metastable entropy-driven thin films. 

Figure 5.2 XRD pattern of reacted T22 phase, exhibiting two different spinel phases as shown in the graph insert. 

Figure 5.3 XRD pattern depicting the <100> textured growth of T22 on (100) silicon. This particular pattern was collected using hybrid incident beam optics and a 1D strip detector to eliminate Ka2 and Kβ peaks for clarity. 

Figure 5.4 Superimposed diffraction patterns from the (111), (220), (200), and (311) T22 film peaks in conjunction with their respective substrate peaks. All substrate peaks were aligned such that their collective make-up duplicates many peaks in a powder diffraction file for Si. This graph was used for indexing and subsequent lattice parameter determination. 

Figure 5.5 EDS map of T22 rocksalt showing the spatial distribution of constituent cations within one fcc sublattice, while oxygen occupies the other fcc sublattice. Observation of each map suggests an overall uniform cation distribution throughout the samples area with minimal cation clustering. 

Figure 5.6 XRD patterns of T22 deposited on (100) Spinel showing a) no film peak present near the (111) Spinel peak, b) a film peak corresponding to (111) rocksalt near (222) Spinel, and c) (200) rocksalt near the (400) Spinel substrate peak. 

Figure 5.7 Powder diffraction pattern of J14C target after 1000 °C reaction in air, held for 12 hours. Rocksalt phase A corresponds very closely in lattice parameter to CaO [126], while rocksalt B is similar to J14. The appearance of tenorite is not surprising because it tends to be the last component to go into the J14 solution [101]. 

Figure 5.8 XRD diffraction pattern of J14C grown on (100) Si at 400 °C. A single film peak is present suggesting textured film growth along the <100> direction, consistent with a rocksalt structure of lattice parameter 4.33Å. 

Figure 5.9 Medium resolution XRD pattern for the (111) and (200) planes of J14C on MgO. Peaks are consistent with that of a relaxed rocksalt thin film of lattice parameter 4.34-4.36Å. There is no evidence of a (111) spinel peak in the 15-18 ° 2θ range. 

Figure 5.10 EDS map of J14C rocksalt showing the spatial distribution of constituent cations within one fcc sublattice, while oxygen occupies the other fcc sublattice. Observation of each map suggests an overall uniform cation distribution throughout the sampling area with minimal cation clustering. 

Figure 5.11 Powder diffraction pattern of J30 post-reaction. Two phases are immediately present: rocksalt and scandia. Based on the intensity ratios of the (111) and (200) rocksalt peaks, between 36 ° and 44 ° 2θ, it is possible that a third spinel phase is present. 

Figure 5.12 2θ-ω scan around the (200) MgO substrate peak. The (200) J30 film peak is located to the left of the substrate, at lower 2θ, indicating a larger out-of-plane d-spacing. 

Figure 5.13 HAADF-STEM image of J30 on (001) MgO viewed down the [010] zone axis. The in-plane lattice parameter, a, of J30 is nearly unchanged from that of the MgO substrate (see panel [010]). By contrast, the out-of-plane c lattice parameter is
Figure 5.14 EDS map of J30 rocksalt showing the spatial distribution of constituent cations within one fcc sublattice, while oxygen occupies the other fcc sublattice. Observation of each map suggests an overall uniform cation distribution throughout the sampling area with minimal cation clustering. Mg appears to be brighter due to the fact that the system is detecting the MgO substrate in addition to the film.

Figure 5.15 Diffraction measurements taken of J30 grown on MgO at time t = 0, 4, 7, 15, and 425 days after growth. There appear to be no changes in the pattern suggesting a thermodynamically metastable film within the timescale of these measurements.

Figure 5.16 Examples of compositions that do not stabilize into a single phase form under bulk synthesis conditions up to 1650 °C. Composition J34 (MgₙNiₙCoₙCuₙZnₙSnₙO, X = 0.1667) (top) depicts a series of phase transformations that appear to approach a single phase rocksalt just above 1650 °C. At 1550 °C two primary phases are present: rocksalt and spinel. At 1650 °C only trace amounts of spinel remain. Composition J35 (MgₙNiₙCoₙCuₙZnₙCrₙO, X = 0.1667)...

Figure 5.17 Omega rocking curves of the (002) peak of the J30 film compared to the MgO substrate. The rocking curves were collected at the optimized 2θ positions for the film and substrate respectively. The substrate has a full-width-half-maximum (FWHM) value of 0.013 ° and the film has a FWHM of 0.018 °.

Figure 5.18 Original skew-symmetric measurement compilation for T22 grown on (100) Si. Comparison with Figure 5.4 shows the same phase present. Discrepancies between the images are a result of different optics used in the measurement.

Figure 6.1 Composition J30 (J14+Sc3+) grown on (100) MgO substrates at incremental deposition temperatures from 150 °C-700 °C. Crystalline growth begins near 300 °C and remains steady with the out-of-plane lattice parameter increasing linearly with temperature. Phase instability appears around 600 °C, and the system relaxes at 700 °C.

Figure 6.2 Plot of J30 lattice constant versus deposition temperature showing a linear increase in c(Å), with in-plane lattice constant remaining pinned to the substrate.

Figure 6.3 Diffraction patterns around the (200) substrate peak for ESO compositions containing a) Sb, b) Ge, c) Cr, and d) Sn.

Figure 6.4 Plot of compositions containing different sixth element additions Sn, Sb, Ge, Cr, and Sc. Each composition has a unique lattice constant trend.

Figure 6.5 J35 series grown on (0001) sapphire and (100) spinel substrates at incremental temperatures from 200 °C - 500 °C at 50 mTorr pO₂. Phase separation occurs at 450 °C. The in-plane relationship of J35 grown on sapphire is shown in supplemental Figure 6.24.

Figure 6.6 Composition J35 grown on a) MgO, b) c-sapphire, and c) Spinel in 50 °C increments from 200 °C-400 °C at 50 mTorr pO₂. In all cases the same lattice trend exists, regardless of substrate.

Figure 6.7 Plot of inter-planar spacing, d₀₀₂, versus deposition temperature for J35 grown on spinel, c-sapphire, and MgO.

Figure 6.8 Lattice distortion as a function of deposition temperature for J14 host: a) diffraction series and b) corresponding lattice parameter vs. temperature. From 200 °C-
350 °C, c remains constantly smaller than the substrate. At 400 °C and higher, c becomes larger than the substrate. Figure 6.9 XRD diffraction pattern around the a) 200 MgO peak depicting complex interference which limits the accuracy of lattice parameter calculation b) the 204 skew-symmetric reflection enabling calculation of lattice parameter, \( c = 4.207\text{Å} \)

Figure 6.10 J14 film grown on a polycrystalline alumina substrate resulting in a polycrystalline film with calculated lattice parameter consistent with the bulk value for cubic symmetry.

Figure 6.11 XRD scan of before and after post deposition anneal of J30 grown at 350 °C.

Figure 6.12 Diffraction series (a) of J35 grown at 10 mTorr pO2 from 250 °C–700 °C with corresponding lattice parameters and inferred instability regions (b).

Figure 6.13 Diffraction series (a) of J35 grown at 30 mTorr pO2 from 300 °C - 500 °C with corresponding lattice parameters and inferred instability regions (b).

Figure 6.14 Scatter plot of c versus deposition temperature for J35 grown on MgO under 10, 30 and 50 mTorr O2. Instability regions shift with temperature and O2 pressure, as evidenced by the appearance of (111) spinel peaks shown in supplementary Figure 6.23.

Figure 6.15 Diffraction series of J35 grown at a) 300 °C in 10 – 50 mTorr O2 with b) the corresponding exponential change in out-of-plane lattice constant versus O2.

Figure 6.16 Plot of c-lattice constant versus oxygen pressure for total pressure and partial pressure series. Regardless of the trend function, both systems experience a decrease in lattice parameter with increasing oxygen content.

Figure 6.17 Plots of c versus deposition temperature for a) the 10mTorr O2 series and b) the 10mTorr O2 series. Again, while there is a slight shift in overall lattice parameter between the pure O2 and the pO2 series, the overall trend of decreasing lattice constant as temperature increases remain the same.

Figure 6.18 Plots of pre and post-annealed lattice parameters for a) J14 at 200 °C and 700 °C and b) J30 at 300 °C, 450 °C, and 700 °C.

Figure 6.19 XRD series depicting the change in out-of-plane lattice parameter for composition \( \text{Mg}_{1-x}\text{Ni}_x\text{O} \) with a) X = 0.01, b) X = 0.5, and c) X = 1. Films are commensurate to the substrate. Vegard’s law predicts bulk lattice parameters for a) 4.212Å and b) 4.187Å. The lattice parameter used for NiO bulk is 4.16Å.

Figure 6.20 Scatter plot of c versus deposition temperature illustrating the trends found in Figure 6.19.

Figure 6.21 Scatter plot comparison \( \text{Mg}_{1-x}\text{Ni}_x\text{O} \) series before and after a 700 °C anneal for one hour in air. The arrows illustrate the relaxation trends for X = 0.5 and X = 1. The X = 0.01 composition has negligible change.

Figure 6.22 Example of an off-axis XRD series for (left) composition J31 and (right) composition J35. In-plane lattice parameters are calculated by fitting these film peaks in conjunction with the (002) film peaks.
Figure 6.23 Diffraction patterns showing the temperature and pressure dependent development of a (111) spinel peak in composition J35 indicating phase separation into a rocksalt + spinel for a) 10mTorr O$_2$, b) 30mTorr O$_2$, and c) 50mTorr O$_2$. Figure 6.24 $\varphi$-scan of J35 grown on c-sapphire. The (104) sapphire planes exhibit three-fold symmetry along <0001>, while J35 exhibits three-fold symmetry along <111> with two directional domains oriented $\pm$ 30 $^\circ$ to the substrate.

Figure B.1 Simplified schematic of a XAFS beamline. The most common (and perhaps most stable) measurement mode is transmission. If the samples do not meet the thickness criteria or contain a dilute species, a fluorescence detector may be a good alternative. Electron-yield is also a measurement mode for XAFS, but avoided entirely because it is never used in this work.

Figure B.2 The absorption and emission process. When x-rays are incident upon an elemental species with a core electron binding energy comparable with that of the light wave, a photoelectron is emitted in the form of a spherical wave. As the wave expands outward, it scatters from neighboring atoms. The interference between the forward and back scattering wave functions give rise to the EXAFS.

Figure B.3 Typical XAFS measurement before processing. The energy range spans 200eV below the known absorption edge of an element (pre-edge) to 800-1200eV above the edge depending on signal-to-noise ratio and whether there is another edge. The XANES region (not analyzed in this work) is approximately -30eV to 50eV around the absorption edge. Above 50eV is considered the EXAFS region.

Figure B.4 Raw data graphs of three consecutive XAFS measurements of the Ni absorber in J14.

Figure B.5 First derivative of a J14-Ni spectrum. The absorption edge should be marked as the first peak regardless of how intense it may be.

Figure B.6 First derivative of the Ni foil spectra. Again, the first peak is chosen to maintain consistency. The intensity of this peak versus the one of J14-Ni is due to the severity of the slope at the onset of the absorption edge.

Figure B.7 $\chi$(k) spectrum showing glitches, denoted by arrows.

Figure B.8 Collective $\chi$(k)spectra for all J14-Ni runs after glitch removal.

Figure B.9 Merged $\chi$(k)spectrum containing all J14-Ni runs. Notice the signal to noise improvement over the individual scans.

Figure B.10 Pre and post-edge fitting for $\mu$(E) normalization.

Figure B.11 Normalized $\mu$(E).

Figure B.12 Background spline fit to $\mu$(E) needed to isolate $\chi$(k).

Figure B.13 Chosen range in $\chi$(k) for Fourier transform and analysis.

Figure B.14 Resulting Fourier transform of the $\chi$(k) spectrum. Most commonly used for model fitting.

Figure B.15 Screenshot of Atoms tab in Artemis showing crystallographic input information.

Figure B.16 Screenshot of Feff output tab in Artemis, providing the calculated lattice positions and potentials with respect to the defined absorber atom. Make sure to change the ipot 0 element to the absorber species of interest.

Figure B.17 Screenshot of the resulting scattering paths from processing the Feff file.
Figure B.18 Fourier transform of $\chi(k)$ for J14 Ni, with a Hanning window between 1.05 and 3.35 Å, containing the individual scattering paths that are using during the fit. 199
Figure B.19 Complete fit to the second nearest neighbor for J-14 Ni. 201
Figure B.20 Snapshot of fit report. $\sigma^2$ values less than 0.009 are ideal, but up to 0.05 is acceptable if static or thermal distortions are expected. A small E0 means the absorption edge was chosen well. Half scattering path lengths determined by fit are in column R. Any severe deviations from what is predicted indicated a fit gone awry. 202
Figure C.1 Series of DSC plots showing the systematic shift in the endothermic reaction peak to higher temperatures as heating rate is increased. 204
Figure C.2 Kissinger Plot of J14. The calculated activation energy for the reaction from multiphase to single phase is calculated to be 767 kJ/mol. 205
Figure C.3 Plot of bulk J14 lattice parameter as a function of temperature. The inset shows the shift in (111) J14 peaks used to calculate lattice parameter. The coefficient of linear thermal expansion was found to be $1.4 \times 10^{-5}$/°C. 206
Figure C.4 Neutron PDF data for compositions J14, J14-10%Zn, and J14+10%Zn from 1-10Å. 208
Figure C.5 PDF of J14 measured at 100K demonstrating the undesirable fitting trend associated with poor sample packing density. 209
1 Introduction

1.1 Materials and Technology

Materials development is the backbone of societal evolution and sustainability [1]–[3]. As a civilization continues to progress, technologies needed for advancement often become materials limited. Thus, it is the grand challenge of scientists and engineers to develop new systems that are innovative enough to set a new technological precedent and maintain application relevance. The standard methodologies in which materials are experimentally developed rely on modification of already well-understood systems to add or improve upon desired properties [4]. Figure 1.1 illustrates this process. The crystal chemistry work done by Pauling, Goldschmidt, and Hume-Rothery [5]–[7] predicted thermodynamically stable structures based on ionic radii of a given chemical constitution. Muller and Roy [8] compiled a significant review of such work, intended as a database for structure predictability, property relationships, and applications. It is on these works that the routes to materials development, both experimental and computational, are based.

![Diagram showing the typical materials development process](image)

*Figure 1.1 The typical materials development process.*

Experimentally, there are numerous routes to materials development, but in this work we will only briefly summarize a few. Chemical substitution is perhaps the most common method used in searching for new materials. It has led to some significant contributions such as the first high temperature superconductor, YCBO [9]. The ionics
community uses substitution to increase charge capacity and improve cycling to find compositions suitable for alternatives to LiCoO$_2$ [10]. Enhanced phase stability and redox properties are found in thermoelectric systems, providing possible design guidelines for oxide converters [11]. The multifunctional materials [12] and multiferroics [13], [14] communities have benefitted from the use of chemical substitution as well.

Epitaxial strain has also proven to be an effective tool for modifying certain properties in a variety of thin film systems, which supersedes that of bulk or lattice-matched equivalents. Experimentalists who play the “strain game” [15] have found scientific improvements, such as enhanced carrier mobility and increased transconductance in high-electron-mobility transistors (HEMT)s [16] and metal-oxide-semiconductor field-effect transistors (MOSFET)s [17]. Inducing compressive strain in superconducting thin films finds that the critical temperature, T$_C$, increases with an increasing out-of-plane lattice constant [18], [19]. Similarly, the ferromagnetic Curie temperature can be tuned though varying tensile strain to the point of temperature saturation above a certain lattice constant [20]. Strain has even given rise to properties non-existent in bulk form, such as the induced room temperature ferroelectricity in SrTiO$_3$ [21].

In addition to experimental approaches, the advent of high-throughput computing has also opened the door to significant contributions from computational researchers. $Ab$ $initio$ methods, such as density functional theory (DFT), and related algorithms—such as CALPHAD [22], [23], AFLOW [24], and CALYPSO [25] —have increased the materials library substantially [26]–[30], increasing opportunities for innovation.
In 2004, Cantor et al. [31] took an alternative approach to conventional methods. They sought to explore the rather sparse, central regions of higher-order phase diagrams where compositions contain near equal amounts of components. In their original work, a 20-component and a 16-component metallic system containing equimolar amounts of elements from essentially every area of the periodic table were synthesized and characterized. Results show each system to be multiphase and brittle; however, a common single primary FCC phase existed—that was chemically rich in transition metals. Using this information, Cantor created six more compositions, each based on an equimolar standard: CrMnFeCoNi. They used this standard, and systematically added various sixth component metals including Cu, Ti, Nb, Ge and V. It was found that all synthesized alloys had a dendritic microstructure with a compositional preference, suggesting the solubility limitations of CrMnFeCoNi, between dendritic and inter-dendritic regions.

Cantor’s work inspired significant research efforts due to the fact that these materials seem to form significantly fewer phases than that dictated by the Gibbs Phase Rule [32], [33]. Yeh, et al. [34] attributed this phenomenon to high mixing entropy, $\Delta S_{\text{mix}}$ ($= -R \sum x_i \ln x_i$), and adopted the term “high entropy alloys” (HEAs). The maximum entropy, dictated primarily by configurational entropy, is at a maximum when components exist in equimolar amounts. They ultimately classified a HEA to be the simultaneous alloying of five or more components where each component makes up between 5% and 35% the total composition. The high configurational entropy
associated with such a composition enhances mutual solubility among constituent species, resulting in minimum phase systems.

More recently [35], two definitions have been accepted as guidelines for the classification of this new family of alloys. The first of which is an extension of the 5 at.%–35 at.% statement to include elements present in ≤ 5 at.% [36]. Constituents are classified into two categories, \( n_{X_i} \) defined as \( n \geq 5 \) and \( 5 \% \leq x_i \leq 35\% \), and \( n_{X_j} \) defined as \( n \geq 0 \) and \( x_j \leq 5\% \). \( n \) corresponds to the number of components, and \( x_m \) is the at.% of the \( m^{th} \) component in the composition. This definition yields three types of compositions: equimolar, non-equimolar, and minor elemental additions. The second definition is based solely on the entropy concept. Here, a HEA is defined as a composition that results in \( \Delta S_{\text{mix}} \geq 1.5R \) where \( R \) is the gas constant, 8.314 J/mol·K. Mixing entropies above this value have a higher affinity for a solid solution [23].

In addition to the stated definitions, the community has agreed upon four core characteristics of HEAs that are expected to affect structure-property relationships (either directly or indirectly). For more rigorous details on the core characteristics of HEAs, please refer to [37], [38].

1. **The high entropy effect.** A equimolar quinary solid solution has a calculated configurational entropy of approximately 1.61R, which is 60% higher than the entropy of fusion of a pure metal. It is therefore expected that entropy enhances the potential for solid solution formation at high temperatures.

2. **Slow kinetics.** HEAs exhibit lower diffusion coefficients compared to their conventional alloys, in turn reducing transformation rates.

3. **Severe lattice distortion.** Differences in atomic size between constituents introduce lattice distortion, potentially changing defect energies as well as kinetics.
4. *The synergistic effect.* Amplified effects can arise from the combined mutual interactions among composing elements in addition to the properties characteristic of constituent elements.

Since their inception, high entropy alloys have gained significant momentum in the movement for materials discovery, particularly for refractory and structural applications [23], [39]–[44]. For example, Cantor’s alloy, CrMnFeCoNi, was found to have a tensile strength between 730 GPa and 1280 GPa, and a fracture toughness exceeding 200 MPa√m. This value increases to greater than 300 MPa√m at 77K. These tensile strength values place the Cr-Mn-Fe-Co-Ni system on a similar level to Ni-Superalloys, Ti-alloys and low alloy steel; however, it far exceeds these materials in fracture toughness [40]. In addition to structural applications, HEAs are currently being investigated for irradiation resistance [45] and magnetic properties [46]–[48].

While HEAs show promise as unique functional materials, an important observation of the literature warrants the following discussion. The premise of HEAs is that high configurational entropy tends to result in significantly less phases than otherwise predicted by the Gibbs Phase Rule through the formation of single phase solid solutions. It becomes obvious that many of the explored compositions, while classified as single phase, contain dendritic microstructures with chemical segregation in their as-cast state. In few instances, a high temperature heat treatment results in the formation of a homogenous single phase [39], implying kinetic limitations. With this information in mind, two main points should be considered. First, it is important to accurately define what it means for a system to be “single phase.” In this work, we shall define a single phase as a physically distinct portion (or whole) of a system that maintains homogenous chemical and physical characteristics, bound by a clear surface [49], [50]. Based on our definition, many HEAs are not single phase. However, this could change for many compositions after a long, high temperature anneal. Second, while these systems do contain high entropies of mixing, the fact that there is preferred compositional variation
throughout these materials indicates that entropy is not at a maximum. There are still other influences on phase formation, such as enthalpy, and thus while the configurational entropy component is substantial it is not necessarily the mechanism that stabilizes these materials [51]. Zhang et al. [52] developed parameters enabling the prediction of solid solution formation in such systems in terms of a defined mathematical expression, $\Delta$, and the enthalpy of mixing, $\Delta H$. Here, $\Delta$ accounts for atomic-size discrepancies and $\Delta H$ predicts chemical compatibility. In their work it is shown that both enthalpy and size mismatch can greatly influence the formation of a solid solution.

Inspired by the pioneering work on HEAs, the present work focuses on the possibility of using entropy as a means to stabilize novel oxide systems. Oxides are a class of ceramics that have proven incredibly diverse in terms of composition variability and applications [9], [53]–[57]. Entropic effects have been extensively studied in a variety of oxides, particularly on the cation distributions of spinel systems [58]–[61]. Navrotsky, et al. [61] treated the cation distribution problem as a chemical equilibrium equation. They made the assumption that the complete disordering process involves one tetrahedral and two octahedral sites, and the maximum configurational entropy corresponds to complete randomization. Interchange enthalpies were calculated based on satisfying equilibrium conditions for several 2-3 and 2-4 spinel compositions, and it was concluded that if cation site preference is small, the distribution becomes entropy mediated. This entropic mediation has significant temperature dependence, particularly at higher temperatures.

While entropy certainly plays a role in stabilizing naturally occurring systems, this is the first attempt to our knowledge at specifically engineering oxides such that entropy is the dominating term that minimizes free energy. The remainder of this work narrates a series of studies investigating routes of entropic stabilization of complex oxide materials with the intent for future exploration of novel structure-property relationships.
1.3 Basic Thermodynamic Principles

Phase stability is dictated by the Gibbs Free Energy, $G$, where in its simplest form is

$$\Delta G(T, P) = \Delta H(T, P) - T\Delta S(T, P).$$  \hspace{1cm} (1.1)

Here, $\Delta H$ is the change in enthalpy (J/mol), $\Delta S$ is the change in total entropy (J/mol·K), and $T$ is the absolute temperature (K). If $\Delta G < 0$, the system will react spontaneously to a more favorable energetic state, and if $\Delta G > 0$, no reaction will occur. The condition for equilibrium, $\Delta G = 0$, is the point when the Gibbs free energy reaches a global energy minimum. When a system in thermodynamic equilibrium experiences a change of state, such as an increase in temperature, it processes towards a new equilibrium condition.

In a multicomponent system, the particular composition must be taken into consideration to obtain the true functional dependence of $\Delta G$, thus $\Delta G(T, P, n_1, n_2, \ldots)$, where $n_i$ corresponds to the number of moles of component $i$. Consider a hypothetical mixing of two arbitrary components, in equal proportion, to form a solid solution:

$$A + B \rightarrow AB.$$

(1.2)

Using the ideal solution model [49], the entropy of mixing is defined using a variant of Boltzmann’s law

$$\Delta S_{mix} = -R \sum_{i=1}^{N} x_i \ln(x_i)$$

(1.3)

where $R$ is the gas constant, 8.314 J/mol·K, and $x_i$ is the mol fraction of component, $i$, in the composition with a total number of components $N$. So for the above reaction

$$\Delta S_{mix} = -R[x_A \ln(x_A) + x_B \ln(x_B)].$$  \hspace{1cm} (1.4)

This relation holds true for all $T$ and $P$, and maximum entropy is achieved when $X_A = X_B$. 
In an ideal solution the enthalpy of mixing, $\Delta H_{mix}$, is zero. Thus any change in the free energy of mixing, $\Delta G_{mix}$, is a result of the change in entropy during the mixing process. This is the simplest definition of entropy-driven stabilization.

In reality, the ideal solution model cannot account for any discrepancies between two identical compositions under the same conditions. Other solution models have been developed expanding upon the ideal model, termed regular solution models. Here, we introduce an “excess” term, defined as the difference between values determined from real mixing and those determined from ideal mixing.

In its simplest form, the regular solution model contains two components: entropy and enthalpy. $\Delta S_{mix}$ for the solution model remains the same as that of the ideal model, defined in (1.3). Therefore, the excess entropy, $\Delta S_{mix}^{xs}$, accumulated from the mixing process of a real solution (as compared to ideal mixing) is zero. Enthalpy, however, is not zero. It is some function of composition

$$\Delta H_{mix}^{xs} = \Delta H_{mix}(x_A, x_B) = a_0 x_A x_B$$

(1.5)

where $a_0$ is some constant. $\Delta H_{mix}$ is the term that considers the bonding preference between components A and B. There are three possible bonding arrangements: AA, BB, or AB = BA. If $\Delta H_{mix} > 0$, AA and BB bonds are preferred and chemical segregation occurs. If $\Delta H_{mix} < 0$, AB type bonding dominates and the system prefers an alloy or intermetallic phase. $\Delta H_{mix} = 0$ corresponds to an ideal solid solution. Accordingly, the sign of $\Delta H_{mix}$ determines whether the departure from ideality is positive or negative, as illustrated in Figure 1.2(a).
Incorporating the excess enthalpy of mixing into the free energy finds

$$\Delta G_{mix}^{xs} = \Delta H_{mix}(x_A, x_B)$$

(1.6)

which is solely a function of composition. Through substitution of (1.3) and (1.5) into (1.1), the total free energy of mixing now becomes

$$\Delta G_{mix} = a_0 x_A x_B + RT[x_A \ln(x_A) + x_B \ln(x_B)]$$

(1.7)
Eqn. (1.7) is depicted for a positive departure from ideality with increasing temperature in Figure 1.2(c). At lower temperatures, the ΔG curve develops additional minima which lead to a miscibility gap in the composition. Here it is demonstrated that the entropy of mixing becomes the dominating term at high temperatures promoting solubility.

Figure 1.2 Variation of thermodynamic mixing properties a) ΔH_{mix}, b) ΔS_{mix}, and c) ΔG_{mix} as a function of composition and temperature for the simplest regular solution model. Adapted from [49].
Phenomenologically, H and S are both functions of temperature. Consider entropy, S, as a function of temperature, T, and pressure, P

\[ S = S(T, P). \]  

(1.8)

The associated differential equation can be written as [49]

\[ dS(T, P) = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP. \]  

(1.9)

Since most processes occur under the constant pressure of 1 atmosphere, dP = 0 and the second term of (1.9) can be immediately eliminated. For any reversible process, the second law of thermodynamics dictates that the heat absorbed, Q, during said process is related to the change in entropy by

\[ \delta Q = TdS \]  

(1.10)

and (1.9) becomes

\[ \delta Q = T \left( \frac{\partial S}{\partial T} \right)_P dT. \]  

(1.11)

The heat capacity at constant pressure, \( C_P \), is defined by the relationship

\[ \delta Q \equiv C_P dT. \]  

(1.12)

Comparing the preceding equations leads to the expression

\[ dS = \frac{C_P}{T} dT. \]  

(1.13)

If we make the assumption that the heat capacity remains constant and no phase transitions occur within the temperature region of interest, integrating both sides of (1.13) yields the final relationship:

\[ S(T) = S_0 + C_P \cdot \ln \frac{T}{T_0}. \]  

(1.14)
Here, $S_0$ is the entropy at temperature $T_0$. Enthalpy is defined as

$$dH = C_p dT.$$  \hspace{1cm} (1.15)

Again assuming the specific heat at constant pressure, $C_p$, is constant, integrating both sides with respect to temperature yields

$$H(T) = C_p T.$$  \hspace{1cm} (1.16)

Inserting (1.14) and (1.16) into the Gibbs free energy equation, we can plot energies of a pure substance as a function of temperature as shown in Figure 1.3.

Figure 1.3 Plot of energy versus temperature, illustrating temperature dependence of enthalpy and Gibbs free energy. Adapted from [62].
It is seen from this plot that enthalpy of a pure substance increases approximately linearly with temperature, while the free energy deceases. The slope of the free energy corresponds to entropy, which becomes more negative at higher temperatures [62]. Thus, higher temperatures favor phases stabilized through the entropy contribution.
2 Experimental Methods

This chapter summarizes the primary experimental methods used throughout this work. Those methods undertaken by collaborators are mentioned throughout the text.

2.1 Powder Processing

Binary oxide powders were mixed in stoichiometric amounts specifically calculated and measured out for particular experiments. For exploratory ESO compositions, component oxides are typically measured such that the amount of each metal species in the mixture was consistently equimolar. In some instances, however, compositions were mixed such that they contained equimolar amounts of each oxide component. This variation is based on attempting the formation of different oxide structures or maintaining disorder on specific lattice sites. A full list of attempted compositions can be found in Appendix A. For experiments pertaining to solubility limits or phase-composition stability, mixing procedures are detailed within the text.

All powders were dry mixed/milled with yttrium-stabilized zirconia (YSZ) media, using a SPEX 8000 Mixer/Mill (L-18728) for 1-2 hours. Powders were pressed into 1.27-3.81 cm diameter pellets using a Carver uniaxial press at forces ranging from 6,000 to 15,000 lbs, followed by a green body density measurement. Pellets were placed on platinum foil-lined zirconia slabs and reacted at temperatures ranging from 700 °C to 1650 °C and soak times between 1 to 50 hours in air. Reacted pellets were measured again for density, and characterized for phase via x-ray diffraction.
2.2 Pulsed Laser Deposition

2.2.1 Target Preparation
Primary target compositions were mixed in stoichiometric amounts, shaker-milled, and pressed into 2.54 cm pellets using a Carver uniaxial press at 12,000 lbs. of force. Each target was fired at 1000 °C in air for 50 hours to ensure a complete reaction. Typical mass loss from water and/or oxygen due to phase transitions ranged from 1%-3% total mass. Each target was phase checked using x-ray diffraction.

2.2.2 PLD-System Setup
Thin films were deposited using a house-built pulsed laser deposition (PLD) chamber with a Coherent, Inc. COMPexPro 102 excimer laser at a wavelength of 248nm. A schematic of the setup is shown in Figure 2.1.

![Figure 2.1 PLD system setup.](image-url)
2.2.3 Thin Film Deposition

Thin films were deposited using the setup shown in Figure 2.1, with the following range of parameters:

- Laser energy: 180–250 mJ
- Energy density: 1–5 J/cm²
- Pulse rate: 6–10 Hz
- Substrate temperature range: 25 °C–700 °C
- Target → substrate distance: 3–6 cm
- Base vacuum pressure: ≤ 5 x 10⁻⁵ Torr
- Oxygen pressure: 0.5–200 mTorr
- Argon pressure: 0–100 mTorr

Substrates were prepared by a solvent rinsing sequence of acetone, isopropanol, and methanol; dried with compressed nitrogen and then UVO cleaned using a Jelight model 42 system for 10 minutes.
2.3 Characterization Techniques

2.3.1 X-Ray Diffraction (XRD)
XRD was done primarily using a PANalytical Empyrean multipurpose diffractometer featuring several interchangeable PreFIX modules. θ-2θ diffraction data for phase identification was recorded using a programmable divergence slit incidence beam optic with a \( \frac{1}{2} \)° anti-scatter slit paired with an X’Celerator 1-D strip detector as the receiving optic. Epitaxial thin films were typically characterized using a double-bounce Ge hybrid monochromator as the incidence beam optic, while a 0.18 ° parallel plate collimator (PPC) with a Xe proportional counter was used as the receiving optic. Textured thin films were characterized using the hybrid optic paired with the 1-D strip detector or the PPC and proportional counter. Phase analysis was carried out using Highscore Plus, while epitaxial films were analyzed using Expert Epitaxy.

Diffraction experiments under non-ambient conditions were performed using a PANalytical Empyrean diffractometer equipped with a HTK-1200N stage, capable of heating to 1200 °C. θ-2θ scans were measured continuously as temperature was increased. Incident beam optics included a programmable divergence slit set to \( \frac{1}{32} \)°, with a \( \frac{1}{2} \)° anti-scatter slit. This system is equipped with a PIXel1D detector.

2.3.2 Differential Scanning Calorimetry (DSC)
DSC measurements were carried out using a Netzsch Jupiter STA 449 F3 equipped with a SiC furnace capable of reaching 1550 °C. A picture of the setup is shown in Figure 2.2. Two Pt crucibles were used: one contained the sample to be measured and the other was an empty reference. Dynamic experiments were done using a heating rate of 5, 10, 15, 20, or 25 °C/min ranging from 25 °C–1300 °C under constant air flow. Prior to each run sequence, the system was calibrated for temperature and sensitivity under specific measurement conditions. Calibration standards are dependent on
crucible type and should always be confirmed in the manual. In the case of Pt, standards used included AgS, BaCO$_3$ and CsCl.

Figure 2.2 DSC sample carrier configuration.
2.4 X-Ray Absorption Fine Structure (XAFS)

2.4.1 Sample Preparation

For transmission mode experiments, sample oxide powders were thoroughly mixed and pre-reacted at 1000 °C in air for 12-48 hours. Powder was checked for phase identification via XRD every 12 hours and remixed to promote a uniform reaction before being replaced in the furnace. The ESO powders were then milled to a fine grain, averaging less than 5μm, using a SPEX 8000 Mixer/Mill.

It is critical that samples are prepared to meet the required thickness for 1 absorption length, defined as 1/μ, where μ is the absorption coefficient. The equation for calculating the absorption coefficient for a material is given by

\[ \mu \approx \rho \sum_i \sigma_i \frac{m_i}{M}, \]  

(2.1)

where ρ is the theoretical density of the sample, σ is the cross section of an absorber species within the sample, and m/M is the weight fraction of said species in the composition. It should be noted that the total cross section is energy dependent, so several μ values for each species are calculated for specific energies just above cation absorption edges, and a weighted average is calculated. The amount of material needed for a 1 cm² sample is averaged based on the absorption energies of each constituent cation. Numerical details are shown in Table 2.1, and all cross-sectional values are found in [63]. Sample powder was weighed accordingly and evenly distributed on a 3 cm x 1 cm piece of 0.7mm thick Kapton tape. The tape was then folded in three parts, sealing the powder and creating a 1 cm² sample, shown in Figure 2.3.
Figure 2.3 Photograph of EXAFS sample. Powder is evenly dispersed on Kapton tape, and folded three times to create a 1 cm x 1 cm square. Kapton is x-ray transparent, and the tri-fold creates the correct number of layers corresponding to appropriate sample thickness.

Table 2.1 Table of EXAFS scattering cross sections, absorption lengths, and calculated mass.

<table>
<thead>
<tr>
<th></th>
<th>Energy</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7709</td>
<td>8333</td>
<td>8979</td>
<td>9659</td>
</tr>
<tr>
<td>$\sigma_{\text{Mg}}$</td>
<td>46.336</td>
<td>36.732</td>
<td>29.367</td>
<td>23.579</td>
</tr>
<tr>
<td>$\sigma_{\text{Co}}$</td>
<td>377.728</td>
<td>308.62</td>
<td>253.701</td>
<td>209.067</td>
</tr>
<tr>
<td>$\sigma_{\text{Cu}}$</td>
<td>57.97</td>
<td>46.649</td>
<td>288.976</td>
<td>239.816</td>
</tr>
<tr>
<td>$\sigma_{\text{Ni}}$</td>
<td>54.791</td>
<td>334.554</td>
<td>277.36</td>
<td>230.33</td>
</tr>
<tr>
<td>$\sigma_{\text{Zn}}$</td>
<td>66.565</td>
<td>54.067</td>
<td>44.3</td>
<td>265.759</td>
</tr>
<tr>
<td>$\sigma_{\text{O}}$</td>
<td>12.563</td>
<td>9.895</td>
<td>7.875</td>
<td>6.306</td>
</tr>
<tr>
<td>$\rho$</td>
<td>6.128</td>
<td>6.128</td>
<td>6.128</td>
<td>6.128</td>
</tr>
<tr>
<td>$\sigma_{\text{Total}}$</td>
<td>622.52</td>
<td>803.53</td>
<td>940.22</td>
<td>1039.73</td>
</tr>
<tr>
<td>$\mu$ (µm$^{-1}$)</td>
<td>0.06</td>
<td>0.08</td>
<td>0.09</td>
<td>0.1</td>
</tr>
<tr>
<td>Absorption Length (µm)</td>
<td>16.064</td>
<td>12.445</td>
<td>10.636</td>
<td>9.618</td>
</tr>
<tr>
<td>Mass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 cm$^2$ Sample (g)</td>
<td>9.84E-03</td>
<td>7.63E-03</td>
<td>6.52E-03</td>
<td>5.89E-03</td>
</tr>
</tbody>
</table>
2.4.2 XAFS Measurements

XAFS was measured at the Advanced Photon Source (APS) beamline 12-BM-B under general user proposals GUP-38672/GUP-40352 and beamline 10-BM-B under general user proposal GUP-46129.

J14 powder samples were measured in transmission mode on 12-BM-B with an energy range of 7500 eV to 12000 eV, covering all absorber cations with the exception of Mg. A labeled photograph of the general setup for beamline 12-BM-B is shown in Figure 2.4. Measurements on this beamline were performed using three sequential FMB Oxford – IC Plus 150mm ionization chambers, filled with 100% N₂, labeled I₀, I₁, and I₂, respectively. The transmission sample, prepared in the way described in section 2.4.1, is located between chambers I₀ and I₁. All metal reference foils are provided by EXAFS Materials [64], and the reference foil for a specific absorber is located between chambers I₂ and I₃. References used in transmission experiments include Co, Ni, Cu, and Zn metals. An example spectra for a Cu metal foil is shown in Figure 2.5.
Figure 2.4 Transmission setup for EXAFS measurements on beamline 12-BM-B at the Advances Photon Source, Argonne National Laboratories.
Figure 2.5 Example of typical absorption spectra obtained from a XAFS measurement using metal reference foils.
3 Entropy-Stabilized Oxides

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3.1 Abstract

Configurational disorder can be compositionally engineered into a mixed oxide by populating a single sublattice with many distinct cations. The formulations promote novel and entropy-stabilized forms of crystalline matter where metal cations are incorporated in new ways. Here, through rigorous experiments, a simple thermodynamic model, and a five-component oxide formulation, we demonstrate beyond reasonable doubt that entropy predominates the thermodynamic landscape, and drives a reversible solid-state transformation between a multi-phase and single-phase state. In the latter, cation distributions are proven to be random and homogeneous. The findings validate the hypothesis that deliberate configurational disorder provides an orthogonal strategy to imagine and discover new phases of crystalline matter and untapped opportunities for property engineering.
3.2 Main Text

A grand challenge facing materials science is the continuous hunt for advanced materials with properties that satisfy the demands of rapidly evolving technology needs. The materials research community has been addressing this problem since the early 1900s when Goldschmidt reported the "the method of chemical substitution" [65], that combined a tabulation of cationic and anionic radii with geometric principles of ion packing and ion radius ratios. Despite its simplicity, this model enabled a surprising capability to predict stable phases and structures. As early as 1926 many of the technologically important materials that remain subjects of contemporary research were identified (though their properties were not known); BaTiO$_3$, AlN, GaP, ZnO, and GaAs are among that list.

These methods are based on overarching natural tendencies for binary, ternary, and quaternary structures to minimize polyhedral distortions, maximize space filling, and adopt polyhedral linkages that preserve electroneutrality [7], [65], [66]. The structure-field maps compiled by Muller and Roy catalogue the crystallographic diversity in the context of these largely geometry-based predictions[67]. There are, however, limitations to the predictive power, particularly when factors like partial covalency, and heterodesmic bonding are considered.

To further expand the library of advanced materials and property opportunities, our community explores possibilities based on mechanical strain[68], artificial layering[69], external fields[70], combinatorial screening[71], interface engineering [72], [73], and structuring at the nanoscale [69], [74]. In many of these efforts, computation and experiment are important companions.

Most recently, high throughput methods emerged as a powerful engine to assess huge sections of composition space [24], [75]–[79] and identified rapidly new Heusler alloys,
extensive ion substitution schemes [80], new 18-electron ABX compounds [81], and new ferroic semiconductors [82].

While these methods offer tremendous predictive power and an assessment of composition space intractable to experiment, they often utilize density functional theory calculations conducted at zero Kelvin. Consequently, the predicted stabilities are based on enthalpies of formation. As such, there remains a potential section of discovery-space at elevated temperatures where entropy predominates the free energy landscape.

This landscape was explored recently by incorporating deliberately five or more elemental species into a single lattice with random occupancy. In such crystals, entropic contributions to the free energy, rather than the cohesive energy, promote thermodynamic stability at finite temperatures. The approach is being explored within the high-entropy-alloy family of materials (HEAs) [31], in which extremely attractive properties continue to be found [40], [83]. In HEAs, however, discussion remains regarding the true role of configurational entropy [84]–[87], as samples often contain second phases, and there are uncertainties regarding short range order. In response to these open discussions, HEAs have been referred to recently as multiple-principle-element alloys [88].

It is compelling to consider similar phenomena in non-metallic systems, particularly considering existing information from entropy studies in mixed oxides. In 1967, Navrotsky and Kleppa showed how configurational entropy regulates the normal-to-inverse transformation in spinels, where cations transition between ordered and disordered site occupancy among the available sublattices [89], [90]. These fundamental thermodynamic studies lead one to hypothesize that in principle, sufficient temperature would promote an additional transition to a structure containing only one sublattice with random cation occupancy. From experiment we know that prior to such
transitions, normal materials melt, however, it is conceivable that synthetic formulations exist that exhibit them.

Inspired by research activities in the metal alloy communities and fundamental principles of thermodynamics we extend the entropy concept to five-component oxides. With unambiguous experiments we demonstrate the existence of a new class of mixed oxides that not only contains high configurational entropy, but is indeed truly entropy-stabilized. Additionally, we present a hypothesis suggesting that entropy-stabilization is particularly effective in a compound with ionic character.

3.2.1 Results

3.2.1.1 Choosing an appropriate experimental candidate

The candidate system is an equimolar mixture of MgO, CoO, NiO, CuO, and ZnO, (which we label as “J14”) so chosen to provide the appropriate diversity in structures, coordination, and cationic radii to test directly the entropic ansatz. The rationale for selection is as follows: the ensemble of binary oxides should not exhibit uniform crystal structure, electronegativity, or cation coordination, and there should exist pairs, e.g., MgO-ZnO and CuO-NiO, that do not exhibit extensive solubility. Furthermore, the entire collection should be isovalent such that relative cation ratios can be varied continuously with electroneutrality preserved at the net cation to anion ration of unity. Tabulated reference data for each component, including structure and ionic radius, can be found in Supplementary Table 3.1.

3.2.1.2 Reversibility

In the first experiment, ceramic pellets of J14 are equilibrated in an air furnace and quenched to room temperature. The temperature spanned a range from $700^\circ$ to $1100^\circ$ C, in 50 °C increments. X-ray diffraction (XRD) patterns showing the phase evolution
are depicted in Figure 3.1. After 700 °C, two prominent phases are observed, rocksalt and tenorite (monoclinic structure). The tenorite phase fraction reduces with increasing equilibration temperature. Full conversion to single-phase rocksalt occurs between 850 °C and 900 °C, after which there are no additional peaks, the background is low and flat, and peak widths are narrow in two-theta (2θ) space.

Reversibility is a requirement of entropy-driven transitions. Consequently, low temperature equilibration should transform homogeneous 1000 °C-equilibrated J14 back to its multiphase state (and vice versa upon heating). Figure 3.1 also shows a sequence of XRD patterns for such a thermal excursion: initial equilibration at 1000 °C, a second anneal at 750 °C, and finally a return to 1000 °C. The transformation from single-phase to multi-phase to single-phase is evident by the x-ray patterns and demonstrates an enantiotropic (i.e., reversible with temperature [91]) phase transition.

Figure 3.1 X-ray diffraction patterns for high entropy formulation J14. J14 consists of an equimolar mixture of MgO, NiO, ZnO, CuO, and CoO. The patterns were collected from a single pellet. The pellet was equilibrated for 2 hours at each temperature in air, then air quenched to room temperature by direct extraction from the furnace. X-ray intensity is plotted on a logarithmic scale and arrows indicate peaks associated with non-rocksalt phases, peaks indexed with (T) and with (RS) correspond to tenorite and rocksalt phases respectively. The two x-ray patterns for 1000 °C annealed samples are offset in 2θ for clarity.
3.2.1.3 Testing entropy though composition variation

A composition experiment is conducted to further characterize this phase transition to the random solid solution state. If the driving force is entropy, altering the relative cation ratios will influence the transition temperature. Any deviation from equimolarity will reduce the number of possible configurations \( \Omega \) \( (S_c = k_B \ln(\Omega)) \), thus increasing the transition temperature. Because \( S_c (x_i) \) is logarithmically linked to mole fraction via \( \sim x_i \ln(x) \), the compositional dependence is substantial.

This dependency underpins our gedankenexperiment where the role of entropy can be tested by measuring the dependency of transition temperature as a function of the total number of components present, and of the composition of a single component about the equimolar formulation.

The calculated entropy trends for an ideal mixture are illustrated in fig. 2(b), which plots configurational entropy for a set of mixtures having \( N \) species where the composition of an individual species is changed and the others (\( N-1 \)) are kept equimolar. Two dependencies become apparent: the entropy increases as new species are added and the maximum entropy is achieved when all the species have the same fraction. Both dependencies assume ideal random mixing. Two series of composition-varying experiments investigate the existence of these trends in formulation J14.

The first experiment monitors phase evolution in five compounds, each related to the parent J14 by the extraction of a single component. The sets are equilibrated at 875 °C (the threshold temperature for complete solubility) for 12 hours. The diffraction patterns in Figure 3.2 (a) show that removing any component oxide results in material with multiple phases. A four-species set equilibrated under these conditions never yields a single-phase material.
The second experiment uses five individual phase diagrams to explore the configurational entropy versus composition trend. In each, the composition of a single component is varied by ±2%, ±6% and ±10% increments about the equimolar composition while the others are kept even. Since any departure from equimolarity reduces the configurational entropy, it should increase transition temperatures to single phase, if that transition is in fact entropy driven. The specific formulations used are given in Supplementary Table 3.2.

Figure 3.2 (c-g) are phase diagrams of composition versus transformation temperature for the five sample sets that varied mole fraction of a single component. The diagrams were produced by equilibrating and quenching individual samples in 25 °C intervals between 825 °C and 1125 °C to obtain the $T_{\text{trans}}$-composition solvus. In all cases equimolarity always leads to the lowest transformation temperatures. This is in agreement with entropic promotion, and consistent with the ideal model shown in Figure 3.2 (b). One set of raw x-ray patterns used to identify $T_{\text{trans}}$ for 10% MgO is given as an example in Supplementary Figure 3.7.
Figure 3.2 Compositional analysis. (a) X-ray diffraction analysis for a composition series where individual components are removed from the parent composition J14 and heat-treated to the conditions that would otherwise produce full solid solution. Asterisks identify peaks from rocksalt while carrots identify peaks from other crystal structures. (b) Calculated configurational entropy in a N-component solid solution as a function of Mol% of the Nth component. (c)-(g) Partial phase diagrams showing the transition temperature to single phase as a function of composition (solvus) in the vicinity of the equimolar composition where maximum configurational entropy is expected. Error bars account for uncertainty between temperature intervals. Each phase diagram varies systematically the concentration of one element.
3.2.1.4 Testing endothermicity

Reversibility and compositionally-dependent solvus lines indicate an entropy driven process. As such, the excursion from multi-phase to single-phase should be endothermic. An entropy-driven solid-solid transformation is similar to melting, thus requires heat from an external source [92]. To test this possibility, the phase transformation in formulation J14 can be co-analyzed with differential scanning calorimetry and in-situ temperature dependent x-ray diffraction using identical heating rates. The data for both measurements are shown in Figure 3.3. Figure 3.3 (a) is a map of diffracted intensity versus diffraction angle (abscissa) as a function of temperature. It covers approximately 4 degrees of 2θ- space centered about the 111 reflection for J14. At a temperature interval between 825 °C and 875 °C, there is a distinct transition to single-phase rocksalt structure –all diffraction events in that range collapse into an intense (111) rocksalt peak.

Figure 3.3 (b) contains the companion calorimetric result where one finds a pronounced endotherm in the identical temperature window. The endothermic response only occurs when the system adds heat to the sample, uniquely consistent with an entropy driven transformation[92]. We note the small mass loss (~1.5%) at the endothermic transition. This mass loss results from the conversion of some spinel (an intermediate phase seen by XRD) to rocksalt, which requires reduction of 3⁺ to 2⁺ cations and release of oxygen to maintain stoichiometry. To address concerns regarding CuO reduction, supplementary Figure 3.8 shows a DSC and TGA curve for pure CuO collected under the same conditions. There is no oxygen loss in the vicinity of 875 °C.
Figure 3.3 Demonstrating endothermicity. (a) \textit{in situ} x-ray diffraction intensity map as a function of $2\theta$ and temperature, and (b) differential scanning calorimetry trace for formulation J14. Note that the conversion to single phase is accompanied by an endotherm. Both experiments were conducted at a heating rate of 5 °C/minute.
3.2.1.5 Testing homogeneity

All experimental results shown so far support the entropic stabilization hypothesis. However, all assume that homogeneous cation mixing occurs above the transition temperature. It is conceivable that local composition fluctuations produce coherent clustering or phase separation events that are difficult to discern by diffraction using a laboratory sealed tube diffractometer. The solvus lines of Figure 3.2(c-g) support random mixing, as the most stable composition is equimolar (a condition only expected for ideal/regular solutions), but it is appropriate to ensure self-consistency with direct measurements. To characterize the cation distributions, extended x-ray absorption fine structure (EXAFS) and scanning transmission electron microscopy with energy dispersive x-ray spectroscopy (STEM EDS) is used to analyze structure and chemistry on the local scale.

EXAFS data were collected for Zn, Ni, Cu, and Co at the Advanced Photon Source 12-BM-B [93], [94]. The fitted data are shown in Figure 3.4; the raw data are given in Supplementary Figure 3.9. The fitted data for each element provide two conclusions: the cation-to-anion first near neighbor distances are identical (within experimental error of ±0.01 Å) and the local structures for each element to approximately seven near neighbor distances are similar. Both observations are only consistent with a random cation distribution.
Figure 3.4 Extended x-ray absorption fine structure. EXAFS measured at APS beamline 12-BM after energy normalization and fitting. Note that the oscillations for each element occur with similar relative intensity and at similar reciprocal spacing. This suggests a similar local structural and chemical environment for each.
As a corroborating measure of local homogeneity, chemical analysis was conducted using a probe-corrected FEI Titan STEM with EDS detection. Thin film samples of J14, prepared by pulsed laser deposition, are the most suitable samples to make the assessment. Details of preparation are given in the methods, and x-ray and electron diffraction analysis for the film are provided in Supplementary Figure 3.10 and Figure 3.11. The sample was thinned by mechanical polishing and ion milling. Figure 3.5 shows a collection of images including 5(a), the high-angle annular dark field signal (HAADF).

In Figure 3.5 (Mg-Zn) the EDS signals for the Kα emission energies of Mg, Co, Ni, Cu, and Zn are shown (additional lower magnification images are included in Supplementary Figure 3.12). All magnifications reveal chemically and structurally homogeneous material.
Figure 3.5 STEM-EDS analysis of J14. (a) is a HAADF image. Panels labeled as Zn, Ni, Cu, Mg and Co are intensity maps for the respective characteristic x-rays. The individual EDS maps show uniform spatial distributions for each element and are atomically resolved.

X-ray diffraction, EXAFS, and STEM-EDS probes are sensitive to 10s of nm, 10s of Å, and 1Å length-scales respectively. While any single technique could be misinterpreted to conclude homogenous mixing, the combination of XRD, EXAFS, and STEM-EDS provide very strong evidence. We note, in particular, the similarity in EXAFS oscillations (both in amplitude and position) out to 12 inverse angstroms. This similarly would be lost if local ordering or clustering were present. Consequently, we conclude with certainty that the cations are uniformly dispersed.
3.2.2 Discussion

The set of experimental outcomes show that the transition from multiple-phase to single-phase in J14 is driven by configurational entropy. To complete our thermodynamic understanding of this system, it is important to understand and appreciate the enthalpic penalties that establish the transition temperature. In so doing, the data set can be tested for self-consistency, and the present data are brought into the context of prior research on oxide solubility.

First we consider an equation relating the initial and final states of the proposed phase transition:

$$\text{MgO}_{(RS)} + \text{NiO}_{(RS)} + \text{CoO}_{(RS)} + \text{CuO}_{(T)} + \text{ZnO}_{(W)} = (\text{Mg, Ni, Co, Cu, Zn})\text{O}_{(RS)}$$ (3.1)

For MgO, NiO, and CoO, the crystal structures of the initial and final states are identical. If we assume that solution of each into the J14 rocksalt phase is ideal, the enthalpy for mixing is zero. For CuO and ZnO, there must be a structural transition to rocksalt upon dissolution from tenorite and wurtzite respectively. If we again assume (for simplicity) that the solution is ideal, the mixing energy is zero, but there is an enthalpic penalty associated with the structure transition. From Davies et al., and Bularzik et al., we know the reference chemical potential changes for the wurtzite-to-rocksalt and the tenorite-to-rocksalt transitions of ZnO and CuO; they are 25 kJ/mol and 22 kJ/mol respectively [95], [96]. If we make the assumption that the transition enthalpies of ZnO(wurtzite)-to-ZnO(rocksalt J14) and CuO(tenorite)-to-CuO(rocksalt J14) are comparable, then the enthalpic penalty for solution into J14 can be estimated. For ZnO and CuO, the transition to solid solution in a rocksalt structure involves an enthalpy change of $(0.2)\cdot(25\ \text{kJ/mol}) + (0.2)\cdot(22\ \text{kJ/mol})$, a total of $+10\ \text{kJ/mol}$. This calculation is based on the product of the mol fraction of each multiplied by the reference transition enthalpy.
This assumption is consistent with the report of Davies et al., who showed that the chemical potential of a particular cation in a particular structure is associated with the molar volume of that structure. Since the rocksalt phases of ZnO and CuO have molar volumes comparable to J14, their reference transition enthalpy values are considered suitable proxies.

In comparison, the maximum theoretically expected configurational entropy difference at 875 °C (the temperature were we observe the transition experimentally) between the single species and the random five-species solid solution is ~15 kJ/mol, 5 kJ/mol larger than the calculated enthalpy of transition. It is possible that the origins of this difference are related to mixing energy as the reference energy values for structural transitions to rocksalt do not capture that aspect.

While the present phase diagrams that monitor $T_{\text{trans}}$ as a function of composition demonstrate rather symmetric behavior about the temperature minima, it is unlikely that mixing enthalpies are zero for all constituents. Indeed, literature reports show that enthalpies of mixing between the constituent oxides in J14 are finite and of mixed sign, and their magnitudes are on the same order as the 5 kJ/mol difference between our calculated predictions [95]. This energy difference may be accounted for by finite and positive mixing enthalpies.

Following this argument, we can achieve a self-consistent appreciation for the entropic driving force and the enthalpic penalties for solution formation in J14 by considering enthalpies of the associated structural transitions and expected entropy values for ideal cation mixing.

As a final test, these predictions can be compared to experiment, specifically by calculating the magnitude of the endotherm observed by DSC at the transition from multiple-phase to single-phase states. Doing so, we find a value ~ 12 kJ/mol (with an
uncertainty of ± 2 kJ/mol). While we acknowledge the challenge of quantitative calorimetry, we note that this experimental result is intermediate to and in close agreement with the predicted values.

Compared to metallic alloys, the pronounced impact of entropy in oxides may be surprising given that on a per/atom basis the total disorder per volume of an oxide seems be lower than in a high-entropy-alloy, as the anion sublattice is ordered (apart from point defects). The chemically uniform sublattice is perhaps the key factor that retains cation configurational entropy. As an illustration, consider a comparison between random metal alloys and random metal oxide alloys.

Begin by reviewing the case of a two-component metallic mixture A-B. If the mixture is ideal, the energy of interaction $E_{A-B} = (E_{A-A} + E_{B-B})/2$, there is no enthalpic preference for bonding, and entropy regulates solution formation. In this scenario, all lattice sites are equivalent and configurational entropy is maximized. This situation, however, never occurs as no two elements have identical electronegativity and radii values. Fig. 6(a) illustrates a two component alloy scenario $A-B$ where species $B$ is more electronegative than $A$. Consequently, the interaction energies $E_{A-A}$, $E_{B-B}$, and $E_{A-B}$, will be different. A random mixture of $A-B$ will produce lattice sites with a distribution of first near neighbors, i.e., species $A$ coordinated to $4-B$ atoms, $2-A$ and $2-B$ atoms, etc. Different coordinations will have different energy values and the sites are no longer indistinguishable. Reducing the number of equivalent sites reduces the number of possible configurations and $S$.

Now consider the same two metallic ions co-populating a cation sublattice, as in Figure 3.6(b). In this case, there is always an intermediate anion separating neighboring cation lattice sites. Again, in the limiting case where only first near neighbors are considered, every cation lattice site is "identical" because each has the same immediate surroundings: the interior of an oxygen octahedron. Differentiation between sites is only apparent when the second near neighbors are considered. From the configurational
disorder perspective, if each cation lattice site is identical, and thus energetically similar to all others, the number of microstates possible within the macrostate will approach the maximum value.

![Figure 3.6 A binary metallic compared to a ternary oxide. A schematic representation of two lattices illustrating how the first near-neighbor environments between species having different electronegativity (the darker the more negative charge localized) for (a) a random binary metal alloy, and (b) a random pseudo-binary mixed oxide. In the latter, near-neighbor cations are interrupted by intermediate common anions.](image)

This crystallographic argument is based on the limiting case where first-near-neighbor interactions predominate the energy landscape, which is an imperfect approximation. Second and third near neighbors will influence the distribution of lattice site energies and the number of equivalent microstates – but the impact will be the same in both scenarios. A larger number of equivalent sites in a crystal with an intermediate sublattice will increase $S$ and expand the elemental diversity containable in a single solid solution and to lower the temperature at which the transition to entropic stabilization occurs. We acknowledge the hypothesis nature of this model at this time.
and the need for a rigorous theoretical exploration. It is presented currently as a possibility and suggestion for future consideration and testing.

We demonstrate that configurational disorder can promote reversible transformations between a multi-phase mixture and a homogeneous solid solution of five binary oxides, which do not form solid solutions when any of the constituents are removed. The outcome is representative of a new class of materials called “entropy-stabilized oxides.” While entropic effects are known for oxide systems, e.g., random cation occupancy in spinels [89], order-disorder transformations in feldspar [97], and oxygen non-stoichiometry in layered perovskites [98], the capacity to actively engineer configurational entropy by composition, to stabilize a quinary oxide with a single cation sublattice, and to stabilize unusual cation coordination values is new. Furthermore, these systems provide a unique opportunity to explore the thermodynamics and structure-property relationships in systems with extreme configurational disorder.

Experimental efforts exploring this composition space are important considering that such compounds will be challenging to characterize with computational approaches minimizing formation energy (e.g., genetic algorithms) or with ad-hoc thermodynamic models (e.g., CALPHAD, Cluster Expansion) [6].

We expect entropic stabilization in systems where near-neighbor cations are interrupted by a common intermediate anion (or vice versa), which includes broad classes of chalcogenides, nitrides, and halides; particularly when covalent character is modest. The entropic driving force—engineered by cation composition—provides a departure from traditional crystal-chemical principles that elegantly predict structural trends in the major ternary and quaternary systems. A companion set of structure-property relationships that predict new entropy-stabilized structures with novel cation incorporation await discovery and exploitation.
3.2.3 Methods

3.2.3.1 Solid-state synthesis of bulk materials

MgO (Alfa Aesar 99.99%), NiO (Sigma Aldrich 99%), CuO (Alfa Aesar 99.9%), CoO (Alfa Aesar 99%) and ZnO (Alfa Aesar 99.9%) are massed and combined using a shaker mill and 3 mm diameter yttrium-stabilized zirconia (YSZ) milling media. To ensure adequate mixing, all batches are milled for at least two hours. Mixed powders are then separated into 0.500 g samples and pressed into 1.27 cm diameter pellets using a uniaxial hydraulic press at 31,000 N. The pellets are fired in air using a Protherm PC442 tube furnace.

3.2.3.2 Temperature evolution of phases

Ceramic pellets of J14 are equilibrated in an air furnace and quenched to room temperature by direct extraction from the hot zone. Phase analysis is monitored by x-ray diffraction using a PANalytical Empyrean x-ray diffractometer with Bragg-Brentano optics including programmable divergence and receiving slits to ensure constant illumination area, a Ni filter, and a 1-D 128 element strip detector. The equivalent counting time for a conventional point detector would be 30s per point at 0.01 ° 2θ increments. Note that all x-ray are collected using substantial counting times and are plotted on a logarithmic scale. To the extent knowable using a laboratory diffractometer, the high-temperature samples are homogeneous and single-phase: there are no additional minor peaks, the background is low and flat, and peak widths are sharp in two-theta (2θ) space.

Temperature dependent diffraction data are collected with PANalytical Empyrean x-ray diffractometer with Bragg-Brentano optics including programmable divergence and
receiving slits to ensure constant illumination area, a Ni filter, and a 1-D 256 element strip detector. The samples are placed in a resistively heated HTK-1200N hot stage in air. The samples are ramped at a constant rate of 5 °C/min with a theta-two theta pattern captured every 1.5 minutes. Calorimetry data are collected using a Netzsch STA 449 F1 Jupiter system in a Pt crucible at 5 °C/min in flowing air.

3.2.3.3 Determining solvus lines

Five series of powders are mixed where the amount of one constituent oxide is varied from the parent mixture J14. Supplementary Table 3.2 List of compositions used to prepare the transition temperature phase diagrams in Figure 3.2(c-g) in the main text lists the full set of samples synthesized for this experiment. Each individual sample is cycled through a heat-soak-quench sequence at 25 °C increments from 850 °C up to 1150 °C. The soak time for each cycle is 2 hours, and samples are then quenched to room temperature in less than 1 minute.

After the quenching step for each cycle, samples are immediately analyzed for phase identification using a PANalytical Empyrean x-ray diffractometer using the conditions identified above. If more than one phase is present, the sample would be put through the next temperature cycle. The temperature at which the structure is determined to be pure rocksalt, with no discernable evidence of peak splitting or secondary phases, is deemed the transition temperature as a function of composition. Supplementary Figure 3.7 shows an example of the collected x-ray patterns after each cycle using the J14L series with +10 % MgO. Once single phase is achieved, the sample is removed from the sequence.

Note that this entire experiment is conducted two times. Initially it is done in 50 °C increments and longer anneals, and to ensure accuracy of temperature values and
reproducibility, it is completed a second time using shorter increments and 25 °C anneals. Findings in both sets are identical to within experimental error bar values. In the latter case, error bars correspond to the annealing interval value of 25 °C.

In the main text relating to Figure 3.2(a) we note that in addition to small peaks from second phases, x-ray spectra for N=4 samples with either NiO or MgO removed show anisotropic peak broadening in 2θ and skewed relative intensities where \( I_{(200)}/I_{(111)} \) is less than unity. This ratio is not possible for the rocksalt structure. Supplementary Table 3.3 shows the result of calculations of structure factors for a random equimolar rocksalt oxide with composition J14. Calculations show that the 200 reflection is the strongest, and that the experimentally measured relative intensities of 111/200 are consistent with calculations. We use this information as a means to best assess when the transition to single phase occurs since the most likely reason for the skewed relative intensity is an incomplete conversion to the single-phase state. This dependency is highlighted in Supplementary Figure 3.7 Expanded view of one XRD temperature ladder showing the progression to single phase with 25 °C annealing steps. Red arrows indicate second phases, green and blue arrows indicate shoulders of second phases associated with wurtsitic and rocksalt structures respectively. Dashed lines highlight relative intensity values. Note that for rocksalt, \( I_{111} \) cannot be larger than \( I_{200} \), thus we can use the relative intensity values as a co-indicator of the final transition to single phase.

3.2.3.4 X-ray absorption fine structure (XAFS)

XAFS is made possible through the general user program at the Advanced Photon Source (APS) in Lemont, IL (GUP-38672). This technique provides a unique way to probe the local environment of a specific element based on the interference between an emitted core electron and the backscattering from surrounding species. XAFS makes no assumption of structure symmetry or elemental periodicity, making it an ideal means to study disordered materials. During the absorption process, core electrons will absorb
incident x-ray energies equal to or greater than their respective binding energies. The emitted photoelectron wave interacts with neighboring species, and the resulting absorption spectrum, displayed as absorption intensity versus incident energy, shows characteristic modulations unique to the target atom and its environment.

Equimolar amounts of the constituent oxides (MgO, NiO, CuO, CoO, and ZnO) are mixed and pre-reacted at 1000 °C in air for 12 hours with intermittent stirring during calcination. The product is mixed into an isopropyl alcohol slurry and ball milled using YSZ media for 24 hours. The powder is then dried in a fume hood at room temperature then re-fired at 1000 °C for 12 hours, then checked via x-ray diffraction to ensure phase purity and that peaks remain narrow and intense. Milled grain size is measured using scanning electron microscopy and determined to average ~10 microns.

A 2:1 powder to 10%PVA/H₂O suspension is mixed continuously to disperse particles within the solution as well as aid in breaking up any agglomerates. Using a Cookson Electronics P-6000 spin coater, thin layers are spun onto 2cm x 2cm square pieces of 25 micron thick Kapton. By trial and observation, it is determined that spinning at 2000 rpm for 1 minute makes a homogenous thin film with the appropriate quantity of particles for XAFS analysis.

APS beamline 12-BM is utilized for its energy range of 4.5keV-23keV, which can probe all cation species except magnesium. Absorption spectra are recorded as a function of energy using a fluorescence set-up[99] with a Canberra 13-element Ge detector. The energies per measurement range from 150eV before the known K absorption edge of the target element to approximately 1000 eV past the edge onset. Supplementary Table 3 lists the cation species of interest and their respective K edges. Simultaneously to the sample fluorescence, reference foils are measured in transmission mode. This enables the energy calibration of the data relative to the theoretical edge of the metal, since compounds tend to have a slight variation in their absorption edge energies. Each
measurement is repeated three times to check for systematic error and to improve signal to noise ratio.

The raw data, shown in Supplementary Figure 3.9 plot the absorption edge and modulations on the post edge background. In order to isolate the EXAFS from these spectra, a background function is fit and subtracted. Energy space is transformed into k-space via the equation [24]:

\[
k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}
\]  

(3.2)

Where \(m\) is electron mass, \(\hbar\) is the reduced Planck's constant, and \(E_0\) is the absorption edge energy. Supplementary Figure 3.9 Relative XAFS spectra as measured at APS beamline 12-BM after background normalization. shows the isolated EXAFS from the measurement. With this data, qualitative conclusions can be made pertaining to the degree of randomness of the cation species. If there were ordering within the system, these spectra would not demonstrate such consistent oscillatory structure and the scattering pathways for individual species would be unique. We limit our current conclusions at this somewhat conservative level as it provides the evidence needed to support a random solid solution.

### 3.2.3.5 Scanning Transmission Electron Microscopy

To best facilitate sample preparation and atomic-resolution analysis in STEM, a single crystal J14 thin film is grown on a \{100\} MgO substrate using pulsed laser deposition (PLD) and thinned to electron transparency. The deposition process used a KrF 248nm excimer laser; with an energy density of 3 J/cm\(^2\), substrate temperature of 600 °C, an oxygen pressure of 50 mTorr, and target to substrate distance of 4 cm. A deposition rate of 6 Hz and 40,000 pulses resulted in an approximately 400 nm thick film. The thin
film sample was used for two reasons: 1) an edge-oriented substrate facilitates imaging along a low index zone axis perpendicular to the thinnest portion of the sample (this can be challenging for random powder specimens), and 2) by capping the thin film with a conductor, one can provide a conductive pathway to mitigate the sample charging that ultimately manifests in image drift. To do so, J14 films were coated with 50 nm of indium tin oxide at room temperature using RF-magnetron sputtering. Indium tin oxide is the preferred conductor as it is mechanically similar to a halide oxide and thus responds comparably to mechanical polishing.

Laser-ablated samples were examined by 4-circle diffraction to assess crystallinity and epitaxy. Supplementary Figure 3.10 shows a theta-two theta and an omega scan for J14 prepared at 600 °C. The films are epitaxial to the MgO substrate (expected since the lattice mismatch is below 1%), and the mosaicity observed in the omega circle is consistent with that present in the MgO substrate. MgO substrates are known to have limited crystal quality (~0.02 ° in omega) due to the flame-fusion technique used to grow them.

An Allied Multiprep polishing system is utilized to prepare a cross-sectional electron microscopy sample by wedge polishing technique [100]. To achieve electron transparency, the polished sample is ion-milled with a Fischione Model 1050 Ion Mill while cooling with liquid nitrogen. A JEOL 2000 S/TEM is used to collect selected area diffraction patterns from the J14 thin film. An aberration corrected FEI Titan G260–300 kV S/TEM equipped with an X-FEG source and an advanced Super-XTM EDS detector system is used to analyze the structure and chemistry of J14. The Titan is operated at 200 kV for (HAADF-STEM) imaging and energy dispersive x-ray spectroscopy (EDS) mapping with the convergence semi-angle set to 15 mrad. The atomic resolution EDS map indicating the position and the arrangement of the ions in the unit cell can be explained by
corresponding HAADF-STEM images in which the atomic columns containing heavier elements are observed brighter.

We note that STEM analysis is also performed on cryogenically fractured J14 powder samples and epitaxial thin films along [001] and [110] zone axes. In all cases STEM EDS analysis revealed no second phases and homogeneous and random elemental distributions within the J14 crystals. The STEM data featured in Figure 3.5 of the main text was chosen since the thin film configuration coated with a capping layer of ITO mitigated charging most effectively and allowed access to near atomic resolution with channeling conditions.

Supplementary Figure 3.11 False colored selected area electron diffraction pattern for formulation J14 taken along a <001> direction. There is no evidence for ordering or second phases. is a selected area diffraction pattern for J14 taken along <001>, the pattern contains no diffraction events that are attributable to second phases or to cation ordering. As such, we conclude single phase on the local scale. Supplementary Figure 3.12 is a lower magnification STEM image showing a wider area view as compared to STEM EDS data in the main text. Two observations are of particular note: 1) the HAADF-STEM image on the left suggests high crystallinity, and 2) the STEM-EDS analysis shows no evidence for chemical segregation or phase separation over a larger range.
3.2.3.6 Configurational entropy in the ideal model

The following derivation describes the method to determine the composition dependence of configurational entropy shown in fig. 2(b) of the main text. An N-species system having composition \( \{x_i\} \) has ideal entropy equal to:

\[
S = -k_B \sum_{i=1}^{N} x_i \log(x_i)
\]  \hspace{1cm} (3.3)

The maximum \( S \) is reached at equicomposition \( x_i = 1/N \) for each \( i \), so:

\[
S_{\text{max}} = -k_B \log(N).
\]  \hspace{1cm} (3.4)

If only one species is varied, composition \( x_1 = x \) for instance, while leaving the other \( N-1 \) species at equicomposition:

\[
x_{i\neq 1} = \frac{1-x}{N-1}.
\]  \hspace{1cm} (3.5)

The ideal entropy becomes:

\[
S = -k_B \left[ x \log(x) + (N-1) \frac{1-x}{N-1} \log\left(\frac{1-x}{N-1}\right)\right] = -k_B \left[ x \log(x) + (1-x) \log\left(\frac{1-x}{N-1}\right)\right].
\]  \hspace{1cm} (3.6)

An expanded plot of entropy versus \( N \) for the entire series is shown in the Supplementary Figure 3.13.
3.3 Acknowledgements

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3.4 Author Contributions

CMR, ES, TB, and JPM designed the experimental plan, performed sample synthesis, and ex situ sample characterization. JPM and SC envisioned and implemented the experiments to test the entropy hypothesis. SC performed thermodynamic calculations for composition dependence of entropy. DH and JLJ performed temperature dependent x-ray diffraction experiments, and ECD and AM conducted TEM investigations.
3.5 Supplementary Materials


<table>
<thead>
<tr>
<th>Binary Oxide</th>
<th>Structure (Space Group)</th>
<th>N</th>
<th>Cation Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>Rocksalt (Fm-3m)</td>
<td>6</td>
<td>0.072</td>
</tr>
<tr>
<td>NiO</td>
<td>Rocksalt (Fm-3m)</td>
<td>6</td>
<td>0.063</td>
</tr>
<tr>
<td>CoO</td>
<td>Rocksalt (Fm-3m)</td>
<td>6</td>
<td>L-0.065 H-0.074*</td>
</tr>
<tr>
<td>CuO</td>
<td>Tenorite (C 2/c)</td>
<td>4</td>
<td>0.073</td>
</tr>
<tr>
<td>ZnO</td>
<td>Wurtzite (P6₃mc)</td>
<td>4</td>
<td>0.074</td>
</tr>
</tbody>
</table>
Table 3.2 List of compositions used to prepare the transition temperature phase diagrams in Figure 3.2(c-g) in the main text.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Composition (x = 0.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J14</td>
<td>Mg$<em>{x}$.Ni$</em>{x}$.Co$<em>{x}$.Cu$</em>{x}$.Zn$_{x}$.O</td>
</tr>
<tr>
<td>J14K-10</td>
<td>Mg$<em>{(x+0.025)}$.Ni$</em>{(x+0.025)}$.Co$<em>{(x+0.025)}$.Cu$</em>{(x+0.025)}$.Zn$_{(x+0.1)}$.O</td>
</tr>
<tr>
<td>J14K-6</td>
<td>Mg$<em>{(x+0.015)}$.Ni$</em>{(x+0.015)}$.Co$<em>{(x+0.015)}$.Cu$</em>{(x+0.015)}$.Zn$_{(x+0.06)}$.O</td>
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<tr>
<td>J14K-2</td>
<td>Mg$<em>{(x+0.005)}$.Ni$</em>{(x+0.005)}$.Co$<em>{(x+0.005)}$.Cu$</em>{(x+0.005)}$.Zn$_{(x+0.02)}$.O</td>
</tr>
<tr>
<td>J14K2</td>
<td>Mg$<em>{(x+0.005)}$.Ni$</em>{(x+0.005)}$.Co$<em>{(x+0.005)}$.Cu$</em>{(x+0.005)}$.Zn$_{(x+0.02)}$.O</td>
</tr>
<tr>
<td>J14K6</td>
<td>Mg$<em>{(x+0.015)}$.Ni$</em>{(x+0.015)}$.Co$<em>{(x+0.015)}$.Cu$</em>{(x+0.015)}$.Zn$_{(x+0.06)}$.O</td>
</tr>
<tr>
<td>J14K10</td>
<td>Mg$<em>{(x+0.025)}$.Ni$</em>{(x+0.025)}$.Co$<em>{(x+0.025)}$.Cu$</em>{(x+0.025)}$.Zn$_{(x+0.025)}$.O</td>
</tr>
<tr>
<td>J14L-10</td>
<td>Mg$<em>{(x+0.1)}$.Ni$</em>{(x+0.025)}$.Co$<em>{(x+0.025)}$.Cu$</em>{(x+0.025)}$.Zn$_{(x+0.025)}$.O</td>
</tr>
<tr>
<td>J14L-6</td>
<td>Mg$<em>{(x+0.06)}$.Ni$</em>{(x+0.015)}$.Co$<em>{(x+0.015)}$.Cu$</em>{(x+0.015)}$.Zn$_{(x+0.1)}$.O</td>
</tr>
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<td>J14L-2</td>
<td>Mg$<em>{(x+0.02)}$.Ni$</em>{(x+0.005)}$.Co$<em>{(x+0.005)}$.Cu$</em>{(x+0.005)}$.Zn$_{(x+0.05)}$.O</td>
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<tr>
<td>J14L2</td>
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</tr>
<tr>
<td>J14L6</td>
<td>Mg$<em>{(x+0.06)}$.Ni$</em>{(x+0.015)}$.Co$<em>{(x+0.015)}$.Cu$</em>{(x+0.015)}$.Zn$_{(x+0.05)}$.O</td>
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<tr>
<td>J14L10</td>
<td>Mg$<em>{(x+0.1)}$.Ni$</em>{(x+0.025)}$.Co$<em>{(x+0.025)}$.Cu$</em>{(x+0.025)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
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<td>J14M-10</td>
<td>Mg$<em>{(x+0.025)}$.Ni$</em>{(x+0.1)}$.Co$<em>{(x+0.025)}$.Cu$</em>{(x+0.025)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
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<td>J14M-6</td>
<td>Mg$<em>{(x+0.015)}$.Ni$</em>{(x+0.06)}$.Co$<em>{(x+0.015)}$.Cu$</em>{(x+0.015)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14M-2</td>
<td>Mg$<em>{(x+0.005)}$.Ni$</em>{(x+0.02)}$.Co$<em>{(x+0.005)}$.Cu$</em>{(x+0.005)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14M2</td>
<td>Mg$<em>{(x+0.005)}$.Ni$</em>{(x+0.02)}$.Co$<em>{(x+0.005)}$.Cu$</em>{(x+0.005)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
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<td>Mg$<em>{(x+0.015)}$.Ni$</em>{(x+0.06)}$.Co$<em>{(x+0.015)}$.Cu$</em>{(x+0.015)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14M10</td>
<td>Mg$<em>{(x+0.025)}$.Ni$</em>{(x+0.1)}$.Co$<em>{(x+0.025)}$.Cu$</em>{(x+0.025)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14N-10</td>
<td>Mg$<em>{(x+0.025)}$.Ni$</em>{(x+0.025)}$.Co$<em>{(x+0.1)}$.Cu$</em>{(x+0.025)}$.Zn$_{(x+0.05)}$.O</td>
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<tr>
<td>J14N-6</td>
<td>Mg$<em>{(x+0.015)}$.Ni$</em>{(x+0.06)}$.Co$<em>{(x+0.015)}$.Zn$</em>{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14N-2</td>
<td>Mg$<em>{(x+0.005)}$.Ni$</em>{(x+0.02)}$.Co$<em>{(x+0.02)}$.Zn$</em>{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14N2</td>
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<tr>
<td>J14N6</td>
<td>Mg$<em>{(x+0.015)}$.Ni$</em>{(x+0.015)}$.Co$<em>{(x+0.06)}$.Cu$</em>{(x+0.015)}$.Zn$_{(x+0.05)}$.O</td>
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<tr>
<td>J14N10</td>
<td>Mg$<em>{(x+0.025)}$.Ni$</em>{(x+0.025)}$.Co$<em>{(x+0.1)}$.Cu$</em>{(x+0.025)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14O-10</td>
<td>Mg$<em>{(x+0.025)}$.Ni$</em>{(x+0.025)}$.Co$<em>{(x+0.025)}$.Cu$</em>{(x+0.1)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14O-6</td>
<td>Mg$<em>{(x+0.015)}$.Ni$</em>{(x+0.015)}$.Co$<em>{(x+0.015)}$.Cu$</em>{(x+0.06)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14O-2</td>
<td>Mg$<em>{(x+0.005)}$.Ni$</em>{(x+0.005)}$.Co$<em>{(x+0.005)}$.Cu$</em>{(x+0.025)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14O2</td>
<td>Mg$<em>{(x+0.005)}$.Ni$</em>{(x+0.005)}$.Co$<em>{(x+0.005)}$.Cu$</em>{(x+0.025)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14O6</td>
<td>Mg$<em>{(x+0.015)}$.Ni$</em>{(x+0.015)}$.Co$<em>{(x+0.015)}$.Cu$</em>{(x+0.06)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
<tr>
<td>J14O10</td>
<td>Mg$<em>{(x+0.025)}$.Ni$</em>{(x+0.025)}$.Co$<em>{(x+0.025)}$.Cu$</em>{(x+0.1)}$.Zn$_{(x+0.05)}$.O</td>
</tr>
</tbody>
</table>
Figure 3.7 Expanded view of one XRD temperature ladder showing the progression to single phase with 25 °C annealing steps. Red arrows indicate second phases, green and blue arrows indicate shoulders of second phases associated with wurtzitic and rocksalt structures respectively. Dashed lines highlight relative intensity values. Note that for rocksalt, $I_{111}$ cannot be larger than $I_{200}$, thus we can use the relative intensity values as a co-indicator of the final transition to single phase.
Table 3.3 Calculated relative intensity ratios for J14.

<table>
<thead>
<tr>
<th>Peak</th>
<th>hkl</th>
<th>d(Å)</th>
<th>2θ(°)</th>
<th>I/Imax</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>111</td>
<td>2.423</td>
<td>37.073</td>
<td>67.0%</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>2.100</td>
<td>43.073</td>
<td>100.0%</td>
</tr>
<tr>
<td>3</td>
<td>220</td>
<td>1.485</td>
<td>62.550</td>
<td>57.6%</td>
</tr>
<tr>
<td>4</td>
<td>311</td>
<td>1.266</td>
<td>74.998</td>
<td>26.4%</td>
</tr>
</tbody>
</table>

Table 3.4 Elements measured at APS beamline 12-BM-B.

<table>
<thead>
<tr>
<th>Element of Interest</th>
<th>Reference Material</th>
<th>K-edge Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>Co Metal Foil</td>
<td>7709</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni Metal Foil</td>
<td>8333</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu Metal Foil</td>
<td>8979</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn Metal Foil</td>
<td>9659</td>
</tr>
</tbody>
</table>
Figure 3.8 DSC and TGA analysis for pure CuO powder collected under the identical conditions as sample J14, 25 °C/minute ramp in flowing air.
Figure 3.9 Relative XAFS spectra as measured at APS beamline 12-BM after background normalization.
Figure 3.10 X-ray analysis in the (left) two-theta and (right) omega circles for a {001} J14 film grown on an MgO single crystal substrate. The rocking curves were collected at the optimized 2θ positions for the film and substrate respectively. Both rocking curves have full-width-half-maximum values of 0.017°.
Figure 3.11 False colored selected area electron diffraction pattern for formulation J14 taken along a <001> direction. There is no evidence for ordering or second phases.
Figure 3.12 A lower magnification HAADF STEM image of formulation J14 (left) and a composite STEM EDS map (right). In this map, the colors correspond to characteristic x-ray intensities where blue=Mg, purple=Co, green=Ni, orange=Cu, and red=Zn. Note that the areal distribution of colors is random and free from clustering.
Figure 3.13 Calculated configurational entropy in a $N$-component solid solution as a function of Mol\% of the $N^{th}$ component. The black dots indicate the compositions with maximum configurations and for each $N$ value occur at the equimolar elemental ratios. The same calculation produced the data in Figure 3.2(b).
Local Structure of the Mg$_{x}$Ni$_{x}$Co$_{x}$Cu$_{x}$Zn$_{x}$O($x=0.2$) Entropy-Stabilized Oxide: An EXAFS Study

Christina M. Rost and Jon-Paul Maria*

*Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695

4.1 Abstract

The realization of entropy stabilized oxides provides an alternative route to novel materials discovery and synthesis. In this chapter, we focus on the measurement and analysis of extended x-ray absorption fine structure of four of the five cation species present in the prototype ESO composition Mg$_{x}$Ni$_{x}$Co$_{x}$Cu$_{x}$Zn$_{x}$O ($x = 0.2$), known as J14. We conclude that the local disorder around each absorbing cation becomes averaged into the unit cell structure as soon as the second coordination shell, and maintain that the ESO composition is a solid solution on the smallest possible length scale.
4.2 Introduction

Recently, the concept of entropy stabilization governing high entropy alloy (HEA) materials has been expanded to the realm of complex oxides [101]. These materials, termed entropy-stabilized oxides (ESOs), follow a similar overarching theme to that of HEAs [31], [51], [85], where in a hypothetical five-component single-phase oxide crystal, the random distribution of the component metals on the cation sublattice produces a level of configurational entropy that exceeds the sum of the formation enthalpies of any intermediate compounds that could otherwise form. The initial publication narrates the development of a rocksalt ESO, henceforth denoted as J14, containing equimolar amounts of Mg, Ni, Co, Cu and Zn binary oxides that was commissioned as the primary subject in a battery of experiments designed to test the entropy stabilization hypothesis. The results of this work show, undoubtedly, that a five component, equimolar oxide system can be stabilized through configurational entropy. While it is well known that entropy plays a significant role in the formation of many naturally occurring materials [58], [59], [61], this work opens doors to exploiting entropy stabilization in additional ceramics. This includes not only more oxide compositions, but also extends to carbides and nitrides, for novel structure-property engineering and application.

While the ESO proof of concept is established, there are still many fundamental questions that need to be addressed. Of particular interest is the degree of disorder, both structural and configurational, that exists on the smallest crystalline length scales possible, i.e., octahedral complex distortions and cation distributions in the next nearest neighbor coordination sphere. From x-ray diffraction (XRD), scanning transmission electron microscopy- energy dispersive spectroscopy (STEM-EDS), and qualitative extended x-ray absorption fine structure (EXAFS), we maintain the ESO rocksalt phase to be a solid solution on all length scales, with no evidence of cation clustering. However, there remains the possibility of distortions that could easily be overlooked due
to small variations that become averaged over a large sampling area. In this work, we follow up on our previous ESO article, outlining, in particular, the measurement and analysis of ESO composition J14 \((\text{Mg}_x\text{Co}_y\text{Ni}_z\text{Cu}_w\text{Zn}_x\text{O, } x = 0.2)\) using EXAFS.

4.3 Experimental Method

Rocksalt ESO samples with equimolar composition \(\text{Mg}_x\text{Ni}_y\text{Co}_z\text{Cu}_w\text{Zn}_x\text{O} \) \((x = 0.2)\) are synthesized using typical solid-state reaction methods. Precursor oxide powders MgO, NiO, CoO, CuO and ZnO are mixed in stoichiometric amounts and ball-milled using yttrium-stabilized zirconia (YSZ) milling media for 8 hours in ethanol. The mixture is dried under standard ambient temperature and pressure (SATP), then placed in a Pt-lined alumina crucible and reacted at 1000 °C in air for a total of 12 hours with intermittent mixing to promote reaction uniformity. Once reacted, the powder is air quenched and hand milled using a mortar and pestle until particle size averaged \(\leq 5 \mu\text{m}\).

The resulting structural phase of the reacted powder is determined using a PANalytical Empyrean x-ray diffractometer, done in Bragg-Brentano geometry using CuKα radiation, and covering a range of \(30 ^\circ < 2\theta < 90 ^\circ\), shown in Figure 4.1.
EXAFS samples are prepared to meet the preferred thickness for one absorption length, defined as $1/\mu$, where $\mu$ is the absorption coefficient. It should be noted that the total cross section is energy dependent, so several $\mu$ values are calculated for specific energies just above cation absorption edges. The amount of J14 needed for a 1-cm$^2$ sample is averaged based on the absorption energies of each constituent cation. The rounded average of material needed to have an averaged thickness of 1 absorption length is 8 g. Numerical details are shown in Table 4.1, and all cross sectional values are found in [63], [102].
Table 4.1 EXAFS cross sections, absorption coefficients, and absorption lengths for energy edged pertaining to Co, Ni, Cu and Zn cations.

<table>
<thead>
<tr>
<th>K-Edge Energy (eV)</th>
<th>$\sigma_{\text{Mg}}$ (cm$^2$/g)</th>
<th>$\sigma_{\text{Co}}$ (cm$^2$/g)</th>
<th>$\sigma_{\text{Cu}}$ (cm$^2$/g)</th>
<th>$\sigma_{\text{Ni}}$ (cm$^2$/g)</th>
<th>$\sigma_{\text{Zn}}$ (cm$^2$/g)</th>
<th>$\sigma_{\text{O}}$ (cm$^2$/g)</th>
<th>$\mu$ (cm$^{-1}$)</th>
<th>$\frac{1}{\mu}$ (µm)</th>
<th>Sample Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7709</td>
<td>46.34</td>
<td>377.73</td>
<td>57.97</td>
<td>54.79</td>
<td>66.56</td>
<td>12.56</td>
<td>622.52</td>
<td>16.06</td>
<td>9.8</td>
</tr>
<tr>
<td>8333</td>
<td>36.73</td>
<td>308.62</td>
<td>46.65</td>
<td>334.55</td>
<td>54.07</td>
<td>9.89</td>
<td>803.53</td>
<td>12.44</td>
<td>7.6</td>
</tr>
<tr>
<td>8979</td>
<td>29.37</td>
<td>253.70</td>
<td>288.98</td>
<td>277.36</td>
<td>44.3</td>
<td>7.87</td>
<td>940.22</td>
<td>10.64</td>
<td>6.5</td>
</tr>
<tr>
<td>9659</td>
<td>23.58</td>
<td>209.07</td>
<td>239.82</td>
<td>230.33</td>
<td>265.76</td>
<td>6.31</td>
<td>1039.73</td>
<td>9.62</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Based on cross sectional information, EXAFS sample powder is weighed and evenly distributed on a 3 cm x 1 cm piece of 0.7-mm thick Kapton tape. The tape is then folded in three parts, sealing the powder and creating a 1 cm$^2$ sample.

EXAFS spectra are collected at beamline 12-BM-B at the Advanced Photon Source, Argonne National Laboratory. Co, Ni, Cu, and Zn K-edges are measured in transmission detection mode using 150mm FMB Oxford Ionization Chambers, with the monochromator detuned 20% for harmonic rejection. Mg is omitted from the experiment as an absorber due to the energetic limitations of the beamline.

Data processing and subsequent analysis is performed using the Demeter software package [103]. K-shell absorption edge energies of each constituent absorber are aligned and calibrated using metal foil standards. Individual scattering paths are generated for each species in J14 using FEFF6 [104] and fit to $\chi(R)$ using least-squares refinement. For a more thorough treatment of the EXAFS technique, please refer to appendix B.
4.4 Results and Discussion

Figure 4.2 (a-d) shows EXAFS spectra, \( \chi(k) \), obtained for Co, Cu, Ni, and Zn absorbers within a single J14 powder sample. Quality data were obtained through a \( k \)-range of up to 13 Å\(^{-1} \), while anything above 13 Å\(^{-1} \) was truncated due to the effects of the next absorber edge. Zn was truncated near 12 Å\(^{-1} \) due to a higher level of spectral anomalies, including noise and glitches. Observation of each \( \chi(k) \) suggests that Co and Ni have similar scattering environments as evidenced by both relative amplitude and phase. Zn exhibits slight differences in amplitude while Cu deviates the most in modulatory structure, particularly at higher \( k \).

The local environmental differences between Co, Ni, Cu, and Zn in J14 is made clearer by taking the Fourier transform of each \( \chi(k) \) from \( k \approx 3.25-11.9 \) Å\(^{-1} \) to obtain the real space function \( \chi(R) \), shown in Figure 4.3(a-d). Overall, each \( \chi(R) \) is consistent with a typical metal-oxide system [93], [105], [106]. The first large peak, between 1-2 Å corresponds to scattering between the absorber and first nearest neighbor oxygen atoms. The second peak, between 2-3 Å pertains to the scattering length between the absorber and the seconds nearest neighbor shell, consisting of metal atoms. Note that all FT plots remain phase-uncorrected, so coordination shell peaks are shifted to lower \( R \) by approximately 0.47-0.5 Å. Disregarding anything below 1 Å due to physical bond length limitations, it can be seen that Co, Ni, and Zn have a first peak of similar position and relative intensity. Cu has a significantly smaller, broader first-shell peak that appears to be shifted to a lower \( R \). Additionally, it should be noted that the second nearest neighbor peak appears to be similar in all cases.
Figure 4.2 EXAFS spectra ($\chi(k)$) for a) cobalt b) copper c) nickel and d) zinc within a single J14 powder sample.
Figure 4.3 The Fourier transform of each EXAFS spectra for a) cobalt, b) nickel, c) zinc, and d) copper. It can be observed that the second coordination shell for each absorber appear to be in the same position in R. Ni, Co and Zn have similar nearest neighbor positions while Cu exhibits both a significant shift to lower R, as well as a decrease in peak amplitude.
Quantitative analysis to obtain EXAFS structural parameters on Ni, Co, Zn, and Cu was done by fitting the first two coordination shells of each FT in J14. This corresponds to a fitting range of around 1 - 3.4 Å in the uncorrected \( \chi(R) \). Each fit has four fitting parameters: amplitude reduction factor \( S_0^2 \), scattering path distance \( R \), mean square relative displacement \( \sigma^2 \), and inner potential shift \( E_0 \). From the Nyquist Criterion [107], there are 11 independent points available for fitting, and in our fitting models we float between 5 and 7 of these points to fit the J14 data.

Based on previous information about J14 obtained through XRD and STEM-EDS, the primary model is setup to be consistent with a rocksalt solid solution, with estimated lattice parameter of 4.24 Å, containing equal amounts of Mg, Ni, Co, Cu and Zn cations. Using Atoms [108], five separate rocksalt structure environments (MgO, NiO, ZnO, CoO, and CuO) were constructed for each absorbing atom and run through FEFF6. Only those scattering paths pertaining to the first two coordination shells—oxygen (1) and metal (2) —within the fitting range were applied. Coordination numbers were constrained to remain consistent with a rocksalt structure: the first coordination shell contains oxygen atoms, while the second coordination shell was randomly divided as evenly as possible among the five cations to simulate a realistic solution-like distribution. Additionally, each shell was constrained such that every atom in said particular shell was equidistant from the absorber regardless of species. Both single and multiple scattering paths were used in each fit in order to accurately account for any scattering above the nearest neighbor coordination sphere.
Table 4.2 lists the average structural parameters obtained from the best fit for the first two coordination shells about each measurable absorber in composition J14, using the solid solution model. $S_0^2$ and $E_0$ are constrained to be the same throughout each individual fit due to the nature of their physical meaning. $S_0^2$ serves to compensate for intrinsic losses in the spectra [109], and in this work we constrain it to remain 1 regardless of absorber. $E_0$ is simply the shift in edge energy needed to align the energy grid of the data to that of the model. In a perfect world, this value would be zero. However, since the choice of $E_0$ during data processing is somewhat arbitrary due to near-edge variations, some difference in value is to be expected. $\sigma^2$ in this work accounts not only for the effect of thermal vibration, but also for local deviations in static disorder that cannot be resolved based on our information limits. If we consider resolution limit in R-space to be limited by $\sim\pi/2\Delta k$ [99], we would be hard pressed to discern any scattering length variations in a given coordination shell $< 0.2\AA$. 
Table 4.2 Results of best fits for Ni, Co, Zn and Cu cations in J14.

<table>
<thead>
<tr>
<th>Absorber</th>
<th>Shell</th>
<th>Element</th>
<th>N</th>
<th>S₀²</th>
<th>σ² (Å²)</th>
<th>E₀(eV)</th>
<th>R(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1</td>
<td>O</td>
<td>6</td>
<td>1.000</td>
<td>0.0064</td>
<td>0.9</td>
<td>2.084</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Ni</td>
<td>1</td>
<td></td>
<td>0.0085</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
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<td></td>
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</tr>
<tr>
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<td>O</td>
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<td>0.2</td>
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<td>0.0101</td>
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<td>6</td>
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<td>0.0067</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
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<td></td>
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<td>Cu</td>
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<td>O</td>
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<td>0.0079</td>
<td>1.0</td>
<td>1.993</td>
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<td>0.0079</td>
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<td>2.220</td>
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<tr>
<td></td>
<td>2</td>
<td>Cu</td>
<td>1</td>
<td></td>
<td>0.0097</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Co</td>
<td>2</td>
<td></td>
<td>0.0097</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg</td>
<td>3</td>
<td></td>
<td>0.0097</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni</td>
<td>3</td>
<td></td>
<td>0.0097</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>3</td>
<td></td>
<td>0.0097</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Ni appears to be in a regular octahedral coordination environment with a bond length of $2.084 \pm 0.005$ Å. This value is highly consistent with the bond length corresponding to pure NiO rocksalt [110]. The second shell information aligns well with the solid solution hypothesis, with an average distance of $2.992 \pm 0.004$ Å from the absorber. Co follows a similar trend to that of Ni, having what appears to be normal octahedral coordination, however the Co-O bond length of $2.089 \pm 0.009$ Å runs smaller than that of the binary J14 component CoO [111]. According to the revised tables of ionic radii by Shannon [112], this average bond length falls in between values stated for the high and low spin states of Co$^{2+}$. The low spin state of six-coordinated Co is noted to exhibit Jahn-Teller distortions [113],[114], so a quick model for a JT-type distortion was fitted to the Co EXAFS spectra. The fit does not result in any significant parameter changes or improvement and thus discerning any such phenomena inconclusive. The Co second shell again exhibits homogeneity among constituent cations with an average scattering length of $2.995 \pm 0.007$ Å. Zn exhibits a slightly smaller oxygen bond length of $2.078 \pm 0.009$, while maintaining a second shell scattering length very similar to that of Co and Ni. The compression of the Zn-O bond can be attributed to compensation from competition of the other M-O bonds in J14.

Cu is a distinct outlier compared to the other three measured absorbers in J14. In this case it was necessary to split the scattering paths of the first coordination shell into two different lengths. The results suggest four planar Cu-O bonds of length $1.993 \pm 0.007$ Å and two axial Cu-O bonds of length $2.22 \pm 0.02$ Å. Both bond lengths and local geometry are consistent with the Jahn-Teller distortion exhibited by Cu in an octahedral environment [115],[116]. The second coordination shell also appears to have a slightly shorter scattering path at $2.979 \pm 0.004$ Å. This is compensated for by the slightly larger value in $\sigma^2$, indicative of some circumferential volume of disorder.

Based on the best fit data to each absorber measured in J14, it appears that while there is a level of local disorder, this disorder begins to “wash out” by the second nearest
neighbor. The average scattering path length between any absorber and this shell is found to be 2.991 Å. In terms of geometry, this second shell length corresponds to one-half the magnitude of the unit cell face diagonal, represented in Figure 4.4. Thus, the calculated average unit cell for J14 based on EXAFS is found to be 4.230 Å. Rietveld analysis [117] of J14 powder yields a lattice parameter of 4.237 Å, proving the EXAFS analysis to be in agreement with XRD results within 0.1%. The results that nearest neighbor oxygen bonds vary with absorbing species, while the next nearest neighbor shell stays consistent suggests the unit cell structure is dictated by the cation sublattice, while oxygen is displaced relative to its coordinated cations.

![Figure 4.4 Diagram depicting 2D, 2 x 1 unit cell of J14 rocksalt. The scattering path characteristic of the second nearest neighbors is the equivalent distance of one half the face diagonal in an FCC unit cell. The total magnitude of the face diagonal, 5.982 Å, corresponds to a cubic lattice parameter of 4.23 Å.](image-url)
To further confirm the hypothesis that J14 has a well-mixed population of cations in the second coordination sphere, clustering models were developed for Ni, Co, Cu, and Zn. Here, the population of a particular species was systematically increased while the remaining cations were decreased as evenly as possible to maintain occupancy of the 12 second shell sites. The graph in Figure 4.5 shows the R-factor, a metric for quality of fit, versus the number of sites occupied by a specific element. It becomes immediately apparent that the quality of fit diminishes as the number of specific cation occupation increases. While specific trends in R-factor vary depending on species, the overall trend suggests that clustering is not of significant occurrence in J14. It remains unclear as to the true configurational pattern of the Mg cation. However the cluster model infers from the nature of the J14 composition that if four of five cations do not show significant signs of clustering, the fifth cation would follow suit. As a control calculation, a simple model using a Zn absorber, whose R-factor changes the least, was constructed where Mg content was varied in the second coordination shell. This results in not only a less satisfactory fit, but it also unrealistically compensates the value for E_0(Zn).
Figure 4.5 R-factor vs. N for Co, Cu, Ni, and Zn cations. The increasing R-factor indicated that as the number of cation species is increased, the fit quality degrades. Based on four of five cations having this trend, it can be assumed to be similar with Mg as well.
4.5 Conclusions

EXAFS was used to observe and understand the average local environment surrounding individual absorbing species within the J14 entropy-stabilized oxide. The subtleties between metal-oxygen bond lengths, not to mention the appearance of possible Jahn-Teller effects with Cu, provide a clear picture that there is a certain level of local disorder within the J14 rocksalt system. Co, Ni and Zn absorbers were found to be six-coordinated to oxygen with respectively uniform bond lengths. The slightly greater mean-square displacement for Co suggests a higher than average distortion, perhaps due to variations in spin state, but this has not been rigorously confirmed. Cu exhibits octahedral distortion consistent with Jahn-Teller, having two longer axial oxygen bonds and four shorter planar bonds. These distortions average out by the next cation shell, resulting in the single cubic lattice parameter measured in XRD. Systematic addition of cation species in the second coordination shell results in the degradation of fit quality as clustering increases, consistent with the complete solid solution model. Based on this study, we know EXAFS is an invaluable technique for understanding ESOs on a local scale. This enables not only confirmation of the “degree of ideality” but also a means to begin understanding the process in which cation octahedra compensate to preserve configurational homogeneity in such systems.

4.6 Acknowledgements

The authors acknowledge support from ARO under contract W911NF-14-0285, the Advanced Photon Source (supported by proposal 40352) for access to synchrotron experiments, and Dr. Sungsik Lee and Dr. Benjamin Reinhart of APS beamline 12-BM regarding collection and interpretation of XAFS data.
4.7 Supplementary Information

4.7.1 Cobalt Solution Model Fit

Name : Fit 27 (zgpl)
Description : fit to J14_Co_Trans_Merge
Figure of merit : 27
Time of fit : 2016-03-16T20:34:25
Environment : Demeter 0.9.20 with perl 5.018002 and using Ifeffit 1.2.11d on Windows 7
Interface : Artemis (Wx 0.9923)
Prepared by :
Contact :

Independent points : 11.5722656
Number of variables : 5
Chi-square : 1364.0334943
Reduced chi-square : 207.5438779
R-factor : 0.0128484
Measurement uncertainty (k) : 0.0010131
Measurement uncertainty (R) : 0.0019715
Number of data sets : 1

Happiness = 100.00/100  color = #D8E796

***** Note: happiness is a semantic parameter and should *****
***** NEVER be reported in a publication -- NEVER! *****

guess parameters:

\[
\begin{align*}
ss0 &= 0.00798245 \pm 0.00094539 [0.00798] \\
delr0 &= -0.02990628 \pm 0.00902818 [-0.02991] \\
enot &= 0.23735948 \pm 0.89922555 [0.2373] \\
ss1 &= 0.00973038 \pm 0.00050234 [0.00973] \\
delr1 &= -0.00335427 \pm 0.00723989 [-0.00335] 
\end{align*}
\]
set parameters:
amp = 0.95668000

Correlations between variables:
delr1 & enot --> 0.8332
enot & delr0 --> 0.7530
delr1 & delr0 --> 0.6436
All other correlations below 0.4

===== Data set >> J14_Co_Trans_Merge << ====================================

: Athena project = C:\Users\SolarDragonSTK\Dropbox\APS 12 BM 2014-3 Run Cycle\J14 Transmission
12BM 2014-3 Analysis\J14_Co_Transmission.prj, 7
: name = J14_Co_Trans_Merge
: k-range = 3.424 - 11.365
: dk = 1
: k-window = hanning
: k-weight = 1,2,3
: R-range = 1 - 3.32
: dR = 0.0
: R-window = hanning
: fitting space = r
: background function = no
: phase correction =
: R-factor by k-weight = 1 -> 0.00991, 2 -> 0.01237, 3 -> 0.01627

name N S02 sigma^2 e0 delr Reff R
==================================================================================================
O.1 6.000 0.957 0.00798 0.237 -0.02991 2.12000 2.09009
Co.1 1.000 0.957 0.00973 0.237 -0.00335 2.99810 2.99475
O.1 O.1 24.000 0.957 0.00798 0.237 -0.05105 3.61910 3.56805
O.1 Co.1 4.000 0.957 0.01771 0.237 -0.00158 3.61910 3.61752
Ni.1 3.000 0.957 0.00973 0.237 -0.00335 2.99810 2.99475
O.1 Ni.1 12.000 0.957 0.01771 0.237 -0.00158 3.61910 3.61752
Mg.1 2.000 0.957 0.00973 0.237 -0.00335 2.99810 2.99475
4.7.2 Copper Solution Model Fit

4.7.2.1 Jahn-Teller Distortion Model

Name : Fit 6 (larzi)
Description : fit to J14_Cu_Trans_Merge
Figure of merit : 6
Time of fit : 2016-03-16T14:12:33
Environment : Demeter 0.9.20 with perl 5.018002 and using Iffefit 1.2.11d on Windows 8
Interface : Artemis (Wx 0.9923)
Prepared by : 
Contact :

Independent points : 11.9052734
Number of variables : 6
Chi-square : 379.5993495
Reduced chi-square : 64.2814179
R-factor : 0.0035073
Measurement uncertainty (k) : 0.0006387
Measurement uncertainty (R) : 0.0013310
Number of data sets : 1
Happiness = 100.00/100  color = #D8E796

***** Note: happiness is a semantic parameter and should *****

***** NEVER be reported in a publication -- NEVER! *****

guess parameters:

\[
\begin{align*}
ss0 &= 0.00792414 \pm 0.00075081 \ [0.00300] \\
delr0 &= -0.12682702 \pm 0.00699959 [-0.12284] \\
enot &= 1.02638825 \pm 0.56364680 \ [1.84364] \\
ss1 &= 0.00975076 \pm 0.0002583 \ [0.00300] \\
delr1 &= -0.01909746 \pm 0.00446833 [-0.01502] \\
delrZ &= 0.09947797 \pm 0.01604369 \ [0.10952]
\end{align*}
\]

set parameters:

\[
\begin{align*}
amp &= 1.00000000
\end{align*}
\]

Correlations between variables:

\[
\begin{align*}
delr1 & \& enot \quad \rightarrow 0.8927 \\
delrZ & \& delr0 \quad \rightarrow 0.8209 \\
enot & \& delr0 \quad \rightarrow 0.8029 \\
delr1 & \& delr0 \quad \rightarrow 0.7347 \\
delrZ & \& enot \quad \rightarrow 0.6904 \\
delrZ & \& delr1 \quad \rightarrow 0.6232
\end{align*}
\]

All other correlations below 0.4

===== Data set >> J14_Cu_Trans_Merge << ============================

: Athena project = C:\Users\SolarDragonSTK\Dropbox\APS 12 BM 2014-3 Run Cycle\J14 Transmission 12BM 2014-3 Analysis\J14_Cu_Transmission.prj, 4
: name = J14_Cu_Trans_Merge
: k-range = 3.464 - 11.885
: dk = 1
: k-window = hanning
: k-weight = 1,2,3
: R-range = 1 - 3.28
: dR = 0.0
: R-window = hanning
: fitting space = r
: background function = no
: phase correction =
: R-factor by k-weight = 1 -> 0.00333, 2 -> 0.00292, 3 -> 0.00427

name N S02 sigma^2 e0 delr Reff R
======================================================================================
O.1 4.000 1.000 0.00792 1.026 -0.12683 2.12000 1.99317
O.1 (clone) 2.000 1.000 0.00792 1.026 0.09948 2.12000 2.21948
Cu.1 1.000 1.000 0.00975 1.026 -0.01910 2.99810 2.97900
O.1 O.1 16.000 1.000 0.00792 1.026 -0.21651 3.61910 3.40259
O.1 O.1 (clone) 8.000 1.000 0.00792 1.026 0.06692 3.61910 3.68602
O.1 Cu.1 2.670 1.000 0.01768 1.026 -0.00883 3.61910 3.61027
O.1 Cu.1 (clone) 1.330 1.000 0.01768 1.026 0.09084 3.61910 3.70994
Co.1 2.000 1.000 0.00975 1.026 -0.01910 2.99810 2.97900
O.1 Co.1 5.330 1.000 0.01768 1.026 -0.00883 3.61910 3.61027
O.1 Co.1 (clone) 2.670 1.000 0.01768 1.026 0.09084 3.61910 3.70994
Mg.1 3.000 1.000 0.00975 1.026 -0.01910 2.99810 2.97900
O.1 Mg.1 8.000 1.000 0.01768 1.026 -0.00883 3.61910 3.61027
O.1 Mg.1 (clone) 4.000 1.000 0.01768 1.026 0.09084 3.61910 3.70994
Ni.1 3.000 1.000 0.00975 1.026 -0.01910 2.99810 2.97900
O.1 Ni.1 8.000 1.000 0.01768 1.026 -0.00883 3.61910 3.61027
O.1 Ni.1 (clone) 4.000 1.000 0.01768 1.026 0.09084 3.61910 3.70994
Zn.1 3.000 1.000 0.00975 1.026 -0.01910 2.99810 2.97900
O1.1 Zn.1 8.000 1.000 0.01768 1.026 -0.00883 3.61910 3.61027
O1.1 Zn.1 (clone) 4.000 1.000 0.01768 1.026 0.09084 3.61910 3.70994
4.7.2.2 Non-Jahn-Teller Distortion Model

Name : Fit 8 (hhfno)
Description : fit to J14_Cu_Trans_Merge
Figure of merit : 8
Time of fit : 2016-03-16T15:00:12
Environment : Demeter 0.9.20 with perl 5.018002 and using Ifeffit 1.2.11d on Windows 8
Interface : Artemis (Wx 0.9923)
Prepared by : 
Contact : 

Independent points : 11.9052734
Number of variables : 5
Chi-square : 1887.6279861
Reduced chi-square : 273.3603532
R-factor : 0.0197708
Measurement uncertainty (k) : 0.0006387
Measurement uncertainty (R) : 0.0013310
Number of data sets : 1

Happiness = 100.00/100  color = #D8E796
***** Note: happiness is a semantic parameter and should *****
***** NEVER be reported in a publication -- NEVER! *****

guess parameters:
ss0 = 0.01755634 # +/- 0.00165842 [0.00300]
delr0 = -0.09297020 # +/- 0.01284987 [-0.12284]
enot = -0.27945802 # +/- 1.07464882 [1.84364]
ss1 = 0.00972566 # +/- 0.00052722 [0.00300]
delr1 = -0.02812660 # +/- 0.00854787 [-0.01502]

set parameters:
amp = 1.00000000

Correlations between variables:
delr1 & enot --> 0.8750
enot & delr0 --> 0.7510
delr1 & delr0 --> 0.6873
All other correlations below 0.4

==== Data set >> J14_Cu_Trans_Merge << ===============================

: Athena project = C:\Users\SolarDragonSTK\Dropbox\APS 12 BM 2014-3 Run Cycle\J14 Transmission
12BM 2014-3 Analysis\J14_Cu_Transmission.prj, 4
: name = J14_Cu_Trans_Merge
: k-range = 3.464 - 11.885
: dk = 1
: k-window = hanning
: k-weight = 1,2,3
: R-range = 1 - 3.28
: dR = 0.0
: R-window = hanning
: fitting space = r
: background function = no
: phase correction =
: R-factor by k-weight = 1 -> 0.01336, 2 -> 0.01896, 3 -> 0.02700

name N S02 sigma^2 e0 delr Reff R
=================================================================

====
O.1 6.000 1.000 0.01756 -0.279 -0.09297 2.12000 2.02703
Cu.1 1.000 1.000 0.00973 -0.279 -0.02813 2.99810 2.96997
4.7.3 Nickel Solution Model Fit

Name : Fit 25 (wtdgs)
Description : fit to J14_Ni_Trans_Merge
Figure of merit : 25
Time of fit : 2016-03-16T13:31:42
Environment : Demeter 0.9.20 with perl 5.018002 and using Ifeffit 1.2.11d on Windows 8
Interface : Artemis (Wx 0.9923)
Prepared by : 
Contact :

Independent points : 11.3203125
Number of variables : 5
Chi-square : 406.9255858
Reduced chi-square : 64.3837762
R-factor : 0.0051347
Measurement uncertainty (k) : 0.0010094
Measurement uncertainty (R) : 0.0020009
Number of data sets : 1

Happiness = 100.00/100  color = #D8E796
***** Note: happiness is a semantic parameter and should *****
***** NEVER be reported in a publication -- NEVER! *****

guess parameters:
enot = 0.93451932 # +/- 0.52060028 [1.00980]
ss0 = 0.00641803 # +/- 0.00053373 [0.00578]
delr0 = -0.03570466 # +/- 0.00526059 [-0.03564]
ss1 = 0.00858580 # +/- 0.00033459 [0.00819]
delr1 = -0.00630712 # +/- 0.00445028 [-0.00643]

set parameters:
amp = 1.00000000

Correlations between variables:
delr1 & enot -- > 0.8019
delr0 & enot -- > 0.7779
delr1 & delr0 -- > 0.6456
All other correlations below 0.4

===== Data set >> J14_Ni_Trans_Merge << ===============================

: Athena project = C:\Users\Christina\Dropbox\APS 12 BM 2014-3 Run Cycle\J14 Transmission 12BM 2014-3 Analysis\J14_Ni_Transmission.prj, 7
: name = J14_Ni_Trans_Merge
: k-range = 3.41 - 11.5
: dk = 1
: k-window = hanning
: k-weight = 1,2,3
: R-range = 1.1 - 3.33
: dR = 0.0
: R-window = hanning
: fitting space = r
: background function = no
: phase correction =
: R-factor by k-weight = 1 -> 0.00365, 2 -> 0.00482, 3 -> 0.00693

name N S02 sigma^2 e0 delr Reff R

==============================================================================
O.1  6.000 1.000 0.00642 0.935 -0.03571 2.12000 2.08430
Ni.1  1.000 1.000 0.00859 0.935 -0.00631 2.99810 2.99179
O.1 O.1  24.000 1.000 0.00642 0.935 -0.06095 3.61910 3.55815
O.1 Ni.1  4.000 1.000 0.01500 0.935 -0.00288 3.61910 3.61622
Co.1  3.000 1.000 0.00859 0.935 -0.00631 2.99810 2.99179
O.1 Co.1  12.000 1.000 0.01500 0.935 -0.00288 3.61910 3.61622
Cu.1  2.000 1.000 0.00859 0.935 -0.00631 2.99810 2.99179
O.1 Cu.1  8.000 1.000 0.01500 0.935 -0.00288 3.61910 3.61622
Mg.1  3.000 1.000 0.00859 0.935 -0.00631 2.99810 2.99179
O.1 Mg.1  12.000 1.000 0.01500 0.935 -0.00288 3.61910 3.61622
Zn.1  3.000 1.000 0.00859 0.935 -0.00631 2.99810 2.99179
O1.1 Zn.1  12.000 1.000 0.01500 0.935 -0.00288 3.61910 3.61622

4.7.4 Zinc Solution Model Fit

Name : Fit 58 (orqvw)
Description : fit to J14_Zn_Merge_Trans
Figure of merit : 58
Time of fit : 2016-03-16T15:40:46
Environment : Demeter 0.9.20 with perl 5.018002 and using Ifeffit 1.2.11d on Windows 8
Interface : Artemis (Wx 0.9923)
Prepared by :
Contact :
Independent points : 11.4775391
Number of variables : 5
Chi-square : 3628.8253761
Reduced chi-square : 560.2166720
R-factor : 0.0144295
Measurement uncertainty (k) : 0.0007474
Measurement uncertainty (R) : 0.0014369
Number of data sets : 1

Happiness = 100.00/100  color = #D8E796
***** Note: happiness is a semantic parameter and should *****
***** NEVER be reported in a publication -- NEVER! *****

guess parameters:
  ss_O_1 = 0.00671528 # +/- 0.00110279 [0.00682]
  delr_O_1 = -0.04195560 # +/- 0.01082275 [-0.02764]
  enot = -0.15806835 # +/- 0.96867490 [1.85251]
  ss_M_1 = 0.00880844 # +/- 0.00065297 [0.00797]
  delr_Zn_1 = -0.00024251 # +/- 0.00859564 [0.00748]

set parameters:
  amp = 1.0000000

Correlations between variables:
  delr_zn_1 & enot --> 0.8040
  enot & delr_o_1 --> 0.7881
  delr_zn_1 & delr_o_1 --> 0.6447
All other correlations below 0.4

===== Data set >> J14_Zn_Merge_Trans << ================================

: Athena project = C:\Users\Christina\Dropbox\APS 12 BM 2014-3 Run Cycle\J14 Transmission 12BM 2014-3 Analysis\J14_Zn_Transmission.prj, 7
name  = J14_Zn_Merge_Trans
k-range  = 3.191 - 11.256
dk  = 1
k-window  = hanning
k-weight  = 1,2,3
R-range  = 1 - 3.27
dR  = 0.0
R-window  = hanning
fitting space  = r
background function  = no
phase correction  =
R-factor by k-weight  = 1 -> 0.01530, 2 -> 0.01274, 3 -> 0.01525

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5 Thin Film Growth of Entropy-Stabilized Oxides Using Pulsed Laser Deposition

Christina M. Rost, David T. Harris, Richard D. Floyd, Everett D. Grimley, James M. LeBeau and Jon-Paul Maria*

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5.1 Abstract

We continue investigations of entropy-stabilized oxides (ESOs), a novel class of multicomponent materials characterized by high configurational disorder of the systemic cation species. The prototype ESO is a rocksalt structure, containing equal amounts of Mg, Co, Cu, Ni, and Zn randomly distributed among the cation sublattice, and oxygen on the anion sublattice. While several single phase bulk ceramics are synthesized through solid state sintering above 875 °C in air, thin films grown via pulsed laser deposition (PLD) enable the expansion of the current composition list. A working hypothesis is that PLD – and in principle other PVD methods – provide sufficient kinetic energy to overcome thermodynamic barriers due to temperature limitations of bulk synthesis, making additional ESOs accessible; including, but not limited to, those compositions that do not form a solid solution under normal synthesis conditions up to 1650 °C and compositions with more than five different cation species. In this work, additional compositions—those only stable in thin film form—are presented.
5.2 Introduction

With entropy-stabilized oxides (ESOs), we are able to systematically evaluate the role of entropy in new materials and show that it can predominate phase stability [101]. If this postulate holds true, introducing additional elements into an equimolar composition should increase the level of configurational disorder, and stabilize an expanded pallet of formulations as homogeneous solid solutions. Work done in the high entropy alloy community reveals such a statement is not so simple. While Cantor’s original work on multicomponent alloys [31] created the high entropy alloy community, he also demonstrated that simply adding additional components to a system, i.e. increasing chemical diversity, did not increase solution stability. In most cases, systems with more than five components formed multiple phases containing chemically segregated fcc structures. Otto, et al. [85] investigated this situation by systematically replacing components in a single phase multicomponent alloy with an elemental analog and observing dissolution trends depending on substituted species. Companion experiments by our group show the limitations of entropy-stabilized solubility, as demonstrated by the example in supplementary Figure 5.16. To date, substantial effort has been put into determining the true mechanisms of phase stability of many different entropy-engineered compositions [22], [51], [86], [118], and the general consensus concludes that there are other driving forces that play a significant role in phase stabilization.

The fundamental difficulty behind entropically-stabilized systems lies within understanding and accounting for the processes that can occur as the system approaches equilibrium with its new surroundings. Equilibrium is defined as the point where the Gibbs free energy,

\[ G = H - TS \]  \hspace{1cm} (5.1)

where H is enthalpy, S is entropy, and T is temperature (K), is at a global minimum [119]. With entropic materials, temperature is increased to the point where the TS term
(for the random occupancy structure) overcomes the formation enthalpy of other cation-ordered structures thus minimizing $G$ in this higher-configurational entropy state. As heating occurs, the system changes to maintain equilibrium with its new environment, and in the ideal scenario, the temperature tipping point at which $G=0$ is accessible. That is to say, $T_{EQ}$ is below the melting point or the range of rapid volatility. For chemical formulations that exhibit substantial elemental diversity, this is likely not the case. In such scenarios populating a single sublattice with very different cations is an interfering energetic encumbrance.

It is intriguing to consider if an alternative synthesis method, assisted by a departure from thermal equilibrium, can overcome this barrier. Physical vapor deposition methods afford this possibility by virtue of energetic bombardment. For example, in pulsed laser deposition (PLD) a high energy density laser pulse creates a dense plasma populated with ions and neutrals with several $10$s of eV [120]. The temperature equivalent to the kinetic energy of a particle can be found using the relation $K.E. = \frac{3}{2} k_B T$, where $k_B$ is the Boltzmann constant ($8.617\times10^{-5}$ eV/K) and $T$ is temperature in Kelvin. Thus, the effective temperature of impeding species is on the order of 10,000K. These effective temperatures provide additional energy that can assist in adatom diffusion, allowing lower substrate temperatures – with equivalent microstructures – when compared to other thermally-based techniques [121]. It is possible that the kinetic energy of incoming species can contribute to the thermodynamic TS term. If it is dissipated rapidly and locally, it is possible that an extreme non-equilibrium state can be formed. In other words, the high effective temperature associated with the ablated species promotes the formation of an entropically-driven structure. While the incoming species exhibit a significantly higher temperature than the substrate, their mass is so small comparatively that they will almost immediately be quenched into their high temperature phase. This is somewhat analogous to quenching a bulk ESO ceramic into its high temperature phase by quickly putting it into contact with a much larger, lower temperature body. If the substrate temperature remains low, the phase should remain metastable. If substrate
reaches a temperature that promotes further diffusion, the system will relax into its intrinsically preferred state, which occurs at low $T$. A diagram depicting this idea is shown in Figure 5.1. In so doing, it is conceivable to circumvent melting.

![Diagram illustrating growth of metastable entropy-driven thin films.](image)

In this work, we explore the high effective temperature regime where entropy is the dominating term in lowering the Gibbs free energy at the time of, and shortly after an adatom condenses on a surface. Using PLD, we are able to synthesize additional ESO compositions that we were unable to create using solid state synthesis techniques up to 1650 °C. The three primary compositions used in this experiment, listed in table 5.1, explore three realms of materials discovery. The first composition serves as an example of a material limited by temperature. The second and third compositions test the solvent capabilities of the original ESO prototype in the context of Pauling and Goldschmidt [7] by introducing cationic strain and valence mismatch, respectively. The following
sections narrate a series of experiments to be considered gateways to further exploration of thin film ESOs.

5.3 Methods

Three primary composition sets were used for this work. The oxide components of each set, listed in Table 5.2 List of components in each composition and their respective molar percentage: T22, J14C, and J30. were combined and shaker milled using YSZ media for 1 hour. The mixed powders are pressed into 1.27 cm pellets using 8,000 lbs of uniaxial force, and reacted at 1000 °C in air for 12 hours. It must be noted that the multiphase ceramic, T22, uses equimolar amounts of each binary oxide component, not equimolar amounts of cations.

<table>
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<tr>
<th>Composition T22</th>
<th>Composition J14C</th>
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Thin films were grown via PLD using a 248nm KrF excimer laser. Si and MgO substrates were cleaned using a solvent rinse sequence of acetone, isopropanol, and methanol followed by a 10 minute UVO treatment. There was no removal of the SiO₂ surface oxide on the Si. Deposition temperature was held at 400 °C; the target-
substrate distance and O₂ pressure remained consistent at 5 cm and 50 mTorr, respectively.

XRD measurements were done on both bulk and thin film samples using a PANalytical Empyrean diffractometer operated at 45kV-40mA. Prefix module configurations varied based on measurement, but included: the programmable divergence slit with the 1D X‘celerator detector, hybrid monochromator with 1D X‘celerator detector, and hybrid monochromator with parallel plate collimator. Thin film samples were prepared for EDS measurements by coating each film with a ~15nm thick layer of Pt or Au metal. EDS was done using a Quanta FEI Quanta 3D FEG SEM set to 20 kV and 8 nA. Between 5 and 10 maps were collected per sample encompassing an area of 3600 μm².

ESO samples were prepared for scanning transmission electron microscopy (STEM) using an FEI Quanta focused ion beam with final thinning at 2 kV. High-angle annular dark-field (HAADF)-STEM was conducted on a probe corrected FEI Titan G2 60-300 kV operated at 200 kV with a beam current of approximately 40 pA, a detector inner semi-angle of 77 mrad, and a probe semi-convergence angle of 13.5 mrad. RevSTEM images were acquired to remove sample drift due to thermal fluctuations, and involved acquisition of between 20 to 40 1024x1024 pixel image frames with a 90° scan system rotation between successive frames [122].
5.4 Results and Discussion

5.4.1 T22-The Multicomponent Alloy

T22 contains a highly diverse set of component oxides; varying in structure, coordination, valence and cationic radii. In accordance with the rules of solubility [7] it is a very reasonable assumption that the combination of these constituents results in anything but a solid solution. This is somewhat expected because several of these components are already known to form spinels, such as ZnGa$_2$O$_4$ and MgGa$_2$O$_4$[123], as well as Zn$_2$TiO$_4$ [124]. This is in part due to the coordination and configurational adaptability of the spinel structure. Figure 5.2 shows the XRD pattern of T22 after a 12 hour heat treatment at 1000 °C in air. It is observed that there are two phases present, as evidenced by peak separations at higher 2θ. Both sets of peaks are consistent with the spinel structure. Through indexing, the lattice parameters are calculated to be 8.38 and 8.34 Å, respectively. While specific cation distribution between the two spinel phases is unknown, it is likely for one phase to be Ga-rich, while the other is Ti-rich.

The T22 ceramic pellet was used to deposit a thin film using PLD on a (100) Si substrate. A symmetric XRD scan about the Si (400) peak from 15 °-105 ° 2θ shows two film peaks present, consistent with either a spinel or rocksalt structure. For phase confirmation, a series of skew-symmetric (off-axis) scans were measured along the <111>, <311>, and <220> directions. The compiled patterns, shown in Figure 5.4, confirm that the film is a rocksalt structure with lattice parameter approximating 4.09Å. The indexed peaks are tabulated in

Table 5.3 Calculation of lattice parameter for T22 rocksalt gown on (100) Si. The series of EDS patterns shown in Figure 5.5 depict the spatial distribution of each cation
species in a 3600 µm² area of T22. While EDS cannot be used to quantify composition due to matrix effects, it suggests that composition is uniform and homogeneous over the length scale of the electron interaction volume and that all elements from the target are present in the film. Figure 5.6 shows both symmetric and skew-symmetric scans of T22 grown on (100) Spinel to examine phase evolution. The film maintains rocksalt structure even though T22 exhibits the same structure when prepared as a bulk ceramic. Note that in Fig 5a there is no film peak in the vicinity of Si (111), the absence of a film reflection here enables one to discriminate between spinel and rocksalt, which can be otherwise difficult to separate.

Table 5.3 Calculation of lattice parameter for T22 rocksalt gown on (100) Si. The calculated standard deviation is ± 0.004.

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<th>k</th>
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Figure 5.2 XRD pattern of reacted T22 phase, exhibiting two different spinel phases as shown in the graph insert.
Figure 5.3 XRD pattern depicting the <100> textured growth of T22 on (100) silicon. This particular pattern was collected using hybrid incident beam optics and a 1D strip detector to eliminate Kα2 and Kβ peaks for clarity.
Figure 5.4 Superimposed diffraction patterns from the (111), (220), (200), and (311) T22 film peaks in conjunction with their respective substrate peaks. All substrate peaks were aligned such that their collective make-up duplicates many peaks in a powder diffraction file for Si. This graph was used for indexing and subsequent lattice parameter determination.
Figure 5.5 EDS map of T22 rocksalt showing the spatial distribution of constituent cations within one fcc sublattice, while oxygen occupies the other fcc sublattice. Observation of each map suggests an overall uniform cation distribution throughout the samples area with minimal cation clustering.
Figure 5.6 XRD patterns of T22 deposited on (100) Spinel showing a) no film peak present near the (111) Spinel peak, b) a film peak corresponding to (111) rocksalt near (222) Spinel, and c) (200) rocksalt near the (400) Spinel substrate peak.
5.4.2 J14C-Strain Induction of J14

Adding a sixth component of a significantly larger cation radius exaggerates this difficulty and thus tests the solvent capabilities of the J14 host. Ca$^{2+}$ has an effective ionic radius of 1.00 Å. As compared to the average cationic radius of the components in J14, 0.725 Å [125], there is a 27.5% difference; well above the ~15% limit for full solubility. Figure 5.7 shows the XRD pattern for J14C after a 12 hour heat treatment at 1000 °C in air. Three phases are present: two rocksalt structures of vastly different lattice parameter and trace amounts of tenorite.

Figure 5.7 Powder diffraction pattern of J14C target after 1000 °C reaction in air, held for 12 hours. Rocksalt phase A corresponds very closely in lattice parameter to CaO [126], while rocksalt B is similar to J14. The appearance of tenorite is not surprising because it tends to be the last component to go into the J14 solution [101].
Figure 5.8 shows the diffraction pattern of J14C grown on (100) Si at 400 °C. Here the film peak suggests a single phase textured film, consistent with (200) rocksalt. With only one peak present it is near impossible to differentiate rocksalt from spinel. However, if we make an assumption that CaO goes into J14 ideally, meaning it maintains the rocksalt structure and equilibrium bond lengths, we can use Vegard’s Law [127] to estimate a lattice parameter and compare it to that calculated from the film peak. From Vegard’s law we obtain the relation for J14C:

\[ a_{J14C} = x(a_{CaO} + a_{CoO} + a_{CuO(RS)} + a_{NiO} + a_{MgO} + a_{ZnO(RS)}) \]  

(5.2)

where a is the cubic lattice parameter for each constituent oxide, and x is the equimolar fraction of each component. Knowing the lattice parameter of J14 to be 4.237 Å and CaO to be 4.8106 Å, we can rewrite (5.2) as

\[ a_{J14C} = xa_{CaO} + (1 - x)a_{J14} \]

(5.3)

and, with \( x = 0.1667 \), find

\[ a_{J14C} = 0.1667(4.8106\text{Å}) + 0.8333(4.237\text{Å}) \approx 4.33\text{Å} . \]

(5.4)

The film peak in Figure 5.8 is located at 41.78 ° 2θ, and through Bragg’s law,

\[ 2d_{hkl}sin\theta = n\lambda \]

(5.5)

where d is the inter-planar lattice spacing, \( \lambda \) is the x-ray wavelength (CuKα = 1.5418 Å), and \( n = 1 \), we estimate \( d_{200} \) to be approximately 2.16 Å. Assuming J14C maintains a rocksalt structure, the corresponding lattice parameter is 4.32 Å, which is in excellent agreement with the Vegard prediction.

Unlike T22, we were unable to confirm the structure of J14C grown on (100) Si using a series of skew symmetric scans. As an additional exercise, J14C was grown on (100) MgO to evaluate the situation of epitaxial growth. XRD patterns of the (111) and (200) planes (see Figure 5.9) confirm epitaxial growth, consistent with rocksalt as there was
no evidence of (111) spinel at low 2θ. The resulting lattice parameters are found to be $a \approx 4.34\text{Å}$ and $c \approx 4.36\text{Å}$, which are consistent with a relaxed, cubic film.

Figure 5.8 XRD diffraction pattern of J14C grown on (100) Si at 400°C. A single film peak is present suggesting textured film growth along the <100> direction, consistent with a rocksalt structure of lattice parameter 4.33Å.
Figure 5.9 Medium resolution XRD pattern for the (111) and (200) planes of J14C on MgO. Peaks are consistent with that of a relaxed rocksalt thin film of lattice parameter 4.34-4.36Å. There was no evidence of a (111) spinel peak in the 15-18 ° 2θ range.
Figure 5.10 EDS map of J14C rocksalt showing the spatial distribution of constituent cations within one fcc sublattice, while oxygen occupies the other fcc sublattice. Observation of each map suggests an overall uniform cation distribution throughout the sampling area with minimal cation clustering.
5.4.3 J30-Valence misfit introduction to J14

The J30 composition follows the same general idea of J14C, but adding Sc$^{3+}$ instead of Ca$^{2+}$. Here, we test the solvent capabilities of J14 by introducing a species of similar ionic radius to the other component cations, but with a different valence. Sc$^{3+}$ has an effective ionic radius of 0.745 Å [112] and would be an appropriate size match compared to the other cations in J14. However, the difference in oxidation state between scandium and J14 should once again limit solubility. The powder XRD pattern shown in Figure 5.11 shows bulk J30 fired at 1000 °C for 12 hours in air. Analysis indicates significant presence of both rocksalt and Sc$_2$O$_3$ phases. Due to peak overlap between spinel and rocksalt structures, we cannot easily rule out any presence of spinel.

![Figure 5.11 Powder diffraction pattern of J30 post-reaction. Two phases are immediately present: rocksalt and scandia. Based on the intensity ratios of the (111) and (200) rocksalt peaks, between 36 ° and 44 ° 2θ, it is possible that a third spinel phase is present.](image)
J30 was deposited on a (100) MgO substrate at 400 °C under 50 mTorr O₂. MgO was chosen due to the low lattice mismatch as predicted from the measured J14 lattice parameter and the estimated bond length associated with the ionic radius of Sc³⁺ and O²⁻. Figure 5.12 shows a 2θ-ω scan about the (200) MgO peak with a film peak to the left of the substrate, indicating a larger out-of-plane lattice parameter, consistent with rocksalt. This was checked by taking a skew symmetric scan aligned to the (111) MgO peak between 15 ° and 20 ° 2θ to confirm the absence of (111) spinel. A film peak near the (111) MgO peak enabled determination that the film was pinned in-plane to the substrate. The presence of well-defined Pendellösung fringes is a result of interference between incident and diffracted waves within the film [128], [129]. These are typically an indicator of a high crystal quality thin film with a smooth, abrupt heteroepitaxial interface. A comparison between film and substrate of the (002) rocking curves is shown in supplementary Figure 5.17.
Figure 5.12 $2\theta$-$\omega$ scan around the (200) MgO substrate peak. The (200) J30 film peak is located to the left of the substrate, at lower $2\theta$, indicating a larger out-of-plane $d$-spacing.

The structure of J30 is further confirmed through the use of HAADF-STEM. HAADF-STEM found the interfaces between the HEO samples and the MgO substrates to be smoothly epitaxial and defect free. The interfaces are abrupt (see Figure 5.13), though there is some evidence for slight intermixing, possibly due to the fact that Mg is present in the film. Indexing of the atom columns [130] allows plotting of $a$ and $c$ lattice parameters directly onto the experimental image on a unit-cell by unit-cell basis. Such measurement finds a $c/a$ lattice parameter ratio of the J30 of 1.0246. By comparison, the $c/a$ lattice parameter ratio of the MgO substrate was measured to be 0.9996. This measurement is in good agreement the X-ray diffraction $c/a$ lattice parameter ratio for the J30 sample.
Figure 5.13 HAADF-STEM image of J30 on (001) MgO viewed down the [100] zone axis. The in-plane lattice parameter, a, of J30 is nearly unchanged from that of the MgO substrate (see panel [010]). By contrast, the out-of-plane c lattice parameter is expanded in the J30 compared to the MgO (see panel [001]). J30 c/a measured to be 26.56 to 25.92 pixel; MgO c/a measured to be 25.85 to 25.86.

Figure 5.14 EDS map of J30 rocksalt showing the spatial distribution of constituent cations within one fcc sublattice, while oxygen occupies the other fcc sublattice. Observation of each map suggests an overall uniform cation distribution throughout the sampling area with minimal cation clustering. Mg appears to be brighter do to the fact that the system is detecting the MgO substrate in addition to the film.
5.4.4 Phase Stability

To determine whether the thin films were thermodynamically metastable, \textit{i.e.}, in a local free energy minimum such that the timescale of any kinetic processes is far beyond our perception, diffraction patterns were recorded periodically over time. As the primary example, the J30 thin film was chosen due to its clear, well-defined diffraction pattern. The hypothesis is that if the system is poorly metastable, any changes that occur can be observed as changes in the diffraction pattern. Figure 5.15 shows x-ray data for J30 collected over the course of 14 months. No discernable changes occur within this timespan. The film peak remains in the same 2\(\theta\) position, with the same relative intensity to the substrate; and the fringing maintains definition and periodicity. In similar context, the skew-symmetric XRD pattern compilation of T22 shown in Figure 5.4 was measured nearly a year after the original scans. Again, peaks remain consistent and there appears to be no change in lattice parameter. The original skew-symmetric scan is shown in supplementary Figure 5.18.
Figure 5.15 Diffraction measurements taken of J30 grown on MgO at time t = 0, 4, 7, 15, and 425 days after growth. There appear to be no changes in the pattern suggesting a thermodynamically metastable film within the timescale of these measurements.
5.5 Conclusions

This work demonstrates the ability to stabilize additional ESOs with pulsed laser ablation not feasible through bulk synthesis. The compositions used are chosen because they incorporate high contrast cations that introduce high charge or cation radius misfits. Composition T22 forms a double spinel system, with lattice constants similar to those of the mineral spinel under normal bulk synthesis conditions. When processed as a thin film, composition T22 condenses into a single-phase rocksalt structure, in which case the highest possible configurational entropy is reached because all cations occupy a single FCC sublattice. Both J14C and J30 also form single-phase rocksalt solid solutions using PLD, showing ultimately that ESOs are particularly effective solid solvents where their cations exist in equal proportions. An initial set of experiments investigates these compositional trends as a function of laser plume dynamics. They suggest that energetic bombardment plays a role in entropy stabilization, but more work is needed before hard conclusions can be drawn. Experimental proof that additional ESO systems can be synthesized in thin film form opens the door to much broader and in-depth research endeavors, elaborated on in the future work.

5.6 Acknowledgements

CMR and JPM acknowledge DTH for the initial synthesis of J30 and J14C compositions and RDF for assistance with EDS measurements. EDG and JML are also acknowledged for their contributions of HAADF-STEM and RevSTEM to the J30 composition. CMR and JPM acknowledge support from ARO under contract W911NF-14-0285. EDG was supported by a National Science Foundation Graduate Research Fellowship (DGE-1252376). JML and EDG acknowledge support from the National Science Foundation (DMR-1350273). Authors acknowledge the use of the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation.
5.7 Supplementary Materials

Figure 5.16 Examples of compositions that do not stabilize into a single phase form under bulk synthesis conditions up to 1650 °C. Composition J34 (MgₓNiₓCoₓCuₓZnₓSnₓO, X = 0.1667) (top) depicts a series of phase transformations that appear to approach a single phase rocksalt just above 1650 °C. At 1550 °C two primary phases are present: rocksalt and spinel. At 1650 °C only trace amounts of spinel remain. Composition J35 (MgₓNiₓCoₓCuₓZnₓCrₓO, X = 0.1667)
At 1000 °C two phases, rocksalt and spinel, are present. At 1600 °C, J35 phase separates into more phases and the spinel phase becomes more prevalent indicating that it is unlikely to reach a single phase state. Spinel phases are denoted by arrows.

Figure 5.17 Omega rocking curves of the (002) peak of the J30 film compared to the MgO substrate. The rocking curves were collected at the optimized 2θ positions for the film and substrate respectively. The substrate has a full-width-half-maximum (FWHM) value of 0.013 ° and the film has a FWHM of 0.018 °.
Figure 5.18 Original skew-symmetric measurement compilation for T22 grown on (100) Si. Comparison with Figure 5.4 shows the same phase present. Discrepancies between the images are a result of different optics used in the measurement.
6 Temperature and Pressure Effects on Six Component Entropy-Stabilized Oxide Thin Films

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6.1 Abstract

We identify an interesting new trend linking out of plane lattice constants to deposition temperature that is expressed strongly in six-component entropy stabilized oxide thin films prepared epitaxially on a variety of single crystal substrates. The trends appear most pronounced when the film formulation contains “misfit cations” that exhibit high radius or charge contrast. The lattice constant changes occur primarily along the out-of-plane direction, irrespective of which crystallographic direction lies parallel. In this work, several experiments that isolate the origins of this lattice parameter trend are presented. The experiments probe the impact of substrate structure, substrate temperature, deposition pressure, and number of components in the film. While a comprehensive explanation cannot be made at this time, the available evidence, in particular x-ray absorption resonant scattering, suggests that valence changes (or at least changing charge distributions) with temperature are enabled in a high entropy host and promote these structural modifications.
6.2 Introduction

The work presented in this chapter was enabled by the new-found ability to stabilize single phase ESO thin films with the addition of high-contrast cations like Sc$^{3+}$, which provides an exciting avenue to search for new and interesting structure-property relationships. It inspires exploration of daughter compositions where a sixth component is added to the J14 host but varies in some other fashion, such as atomic mass, preferred oxidation state, electronic structure, radius, or bonding character. In chapter 5, preparations of J30 (J14+Sc$^{3+}$) by laser ablation resulted in epitaxial thin films with unusually high crystalline perfection, i.e., narrow line widths and robust Pendellösung fringes. These initially encouraging results prompted follow-on experiments to explore additional structural optimizations. The first experiment varied deposition temperatures between 150 °C - 700 °C. Figure 6.1 shows a series of 2θ-ω scans around the (200) MgO substrate peak for J30 films grown at incremental substrate temperatures spanning this range, all other parameters identical. From these measurements, it appears that the out-of-plane lattice parameter, c, increases linearly with deposition temperature. From 300 ° to 500 °C, J30 grows as a single phase epitaxial film. At temperatures higher than 500 °C the system begins to phase relax, and by 700 °C the material reverts to the “metastable” cubic structure, i.e., the structure (as we show below) we associate with the entropy stabilized situation. This trend is illustrated in terms of calculated lattice parameter as a scatter plot in Figure 6.2.

This is an unusual result considering the large lattice constant change for an isocompositional film series grown on the same substrate with constant O$_2$ pressure, the only difference in deposition is temperature. Similar effects have been witnessed in recent years. Wei, et al. [131] found that the c-axis lattice constant in LaNiO$_3$ grown on LaAlO$_3$ is tunable via O$_2$ pressure and growth temperature. They found that out-of-plane lattice constant increased by 0.6% with decreasing O$_2$ from 375 mTorr to 37.5 mTorr,
and decreased 0.2% with decreasing deposition temperature from 720 °C to 530 °C. They attribute such phenomena to oxygen-related effects, and consider lattice constant changes a manifestation of internal strain mediated by O²⁻ vacancies. Wang, et al. [132] found that the c-plane lattice constant in Ba₀.₅Sr₀.₅TiO₃ increased by 1.8% when deposition pO₂ was decreased from 300 mTorr to 7.5x10⁻³ mTorr O₂, suggesting again that oxygen deficiency plays a role in lattice tunability. Upon annealing that lattice constants in these films returned to bulk parameters, consistent with an increase oxygen stoichiometry [133]. A separate study with SrRuO₃ [134] also found a lattice constant dependence on deposition temperature and pressure; however, in this case the changes were attributed to energetic bombardment and intrinsic crystal quality, and were not related to oxygen stoichiometry. The higher crystal quality provided by higher temperature enables a larger penetration depth for incident species. Higher temperature also promotes greater atom mobility providing more uniform and systematic strain.

While the lattice constant trends in the present case are similar, their magnitudes are substantially larger than in many of the previous studies, and the contrast in depositions that creates them is much less dramatic, i.e., a “strain” of 2.5% produced by an excursion from 300 °C to 500 °C. This suggests an alternative mechanism or a much greater susceptibility to a similar one.

In this chapter, we explore the relationship between lattice constant, substrate, and deposition conditions in entropy stabilized oxide thin films and develop an initial set of hypotheses to explain them. Several questions arise when contemplating possible avenues of exploration: Does a similar trend occur in other sixth component compositions? Does the substrate have an influence on the trends? Can we disentangle the effects of total pressure, bombardment, and oxygen partial pressure? How important are the elemental properties of constituent number six? This chapter explores these questions systematically to begin studying the true nature of ESO films grown via
PLD. While influential parameters are found and initial hypotheses are proffered, the understanding remains nascent and the subject of future research.

Figure 6.1 Composition J30 (J14+Sc3+) grown on (100) MgO substrates at incremental deposition temperatures from 150 °C-700 °C. Crystalline growth begins near 300 °C and remains steady with the out-of-plane lattice parameter increasing linearly with temperature. Phase instability appears around 600 °C, and the system relaxes at 700 °C.
Figure 6.2 Plot of J30 lattice constant versus deposition temperature showing a linear increase in c(Å), with in-plane lattice constant remaining pinned to the substrate.
6.3 Methods

Laser ablation targets of several six-component compositions (J14+X, where X = Sc^{3+}, Sb^{3+}, Sn^{4+}, Cr^{3+} oxides, or Ge metal) were synthesized using standard powder processing techniques. The formulations, listed in Table 6.1, were chosen to maintain the equimolar state. Powders were mixed in a shaker mill with 3mm yttrium-stabilized zirconia (YSZ) milling media for two hours. Powders were pressed into 1.27 cm pellets using 8,000lbs of uniaxial force and reacted at 1000 °C for 12 hours in air. Thin films were grown using pulsed laser deposition (PLD) on single crystal substrates (100) MgO, (100) Spinel, and (0001) Sapphire. Substrates are prepared using a solvent rinsing sequence of acetone, isopropanol, and methanol, followed by a 10 minute UVO treatment. Films are deposited using a 248nm KrF laser set consistently for 250 mJ pulses focused to ~4 J/cm² at a rate of 6Hz. Target to substrate distance was held at 5 cm. For temperature series depositions, the O₂ pressure was set to 10, 30, and 50 mTorr. For pressure series work, the substrate temperature was held constant at 300 °C while O₂ was incrementally varied between 10 and 50 mTorr. An equivalent pressure series was done to correlate possible bombardment effects using an O₂/Ar gas mixture such that the chamber was held constant at 50 mTorr. O₂ was incrementally varied between 10 and 50 mTorr, while Ar was varied from 40 to 0 mTorr, respectively. Since Ar is inert, will have minimal impact on film composition. X-ray diffraction was used to characterize deposited thin films with a PANalytical Empyrean laboratory diffractometer.
As a starting point, we set out to include sixth species additions to J14 that have unique elemental characteristics and maintain the size criteria of less than 15% radii difference. Antimony, Sb$^{3+}$, varies from Sc$^{3+}$ in ionic radius by only 1.9% [112] but is nearly triple the relative atomic mass [135]. Because structural stability is related to ionic radius, we would expect Sb to follow the same lattice trend presented by Sc. Ge$^{2+}$ exhibits covalent character when bonded to oxygen [136]. The directionality associated with covalent character should have a consistent effect on trending lattice distortions unique to the Ge-containing composition. Sn$^{2+}$ contains lone pairs [137], [138]. Lone pairs are non-bonding valence electrons that give rise to vacant ligand sites resulting in deviations from ideal coordination geometry. It should be noted that Sb, Ge, and Sn can exist in more than one possible oxidation state [139]. However, we assume the valence state whose corresponding ionic radius matches closest with that of the J14 average. Cr$^{x+}$ holds a very large range of possible valence states, from 2+ through 6+ [140]. The variability in valence state corresponds to possible changes in ionic radius up to 45%. Correspondingly, changes in oxidation state will alter bond lengths and lattice parameters, and in the most extreme cases destabilize the structure. Collectively each of the above elements has a unique property that could influence structural characteristics. In turn, these characteristics could manifest lattice trends that we may be able to back relate to the sixth element.

Table 6.1 List of compositions used in this study.

<table>
<thead>
<tr>
<th>Mol%</th>
<th>J30</th>
<th>J31</th>
<th>J34</th>
<th>J35</th>
<th>J36</th>
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<td>ScO$_{1.5}$</td>
<td>SbO$_{1.5}$</td>
<td>SnO$_2$</td>
<td>CrO$_{1.5}$</td>
<td>Ge(metal)</td>
</tr>
</tbody>
</table>
6.4 Results and Discussion

6.4.1 Lattice Trends of other Sixth Component Compositions

Figure 6.3 (a-d) shows the x-ray data for the first experiment where each composition was prepared over a range of substrate temperatures. Diffraction data is shown in each case over an angular range proximal to the (200) MgO substrate peak for compositions containing Sc, Sn, Sb, Ge and Cr. Figure 6.4 summarizes the out-of-plane lattice constants for all films in a single master plot. From these data, several observations can be made:

- All films retain the single-phase rocksalt structure and the film quality (as evidenced by x-ray peak widths) remains high for all compositions, irrespective of component six. This is interesting considering that these cations (at least at room pressure) are reluctant to exist as regular edge-shared octahedra;
- The out of plane lattice constant for all formulations is strongly temperature dependent, however, the directionality of the dependence can be compressive or tensile;
- Skew-symmetric x-ray scans show that all films are pseudomorphic up to temperatures where their lattice constants “relax”, examples of such scans are shown in additional supplementary Figure 6.22;
- The minimum temperature for crystalline film growth depends on component six, as does the maximum temperature before relaxation;
- Finally, note that none of the above compositions (with the possible exception of J14+Sn) could be stabilized using powder synthesis and solid state reactions.
Figure 6.3 Diffraction patterns around the (200) substrate peak for ESO compositions containing a) Sb, b) Ge, c) Cr, and d) Sn.
Figure 6.4 Plot of compositions containing different sixth element additions Sn, Sb, Ge, Cr, and Sc. Each composition has a unique lattice constant trend.
6.4.2 Investigating Substrate Effects in J14+Cr Growth Trend

A common factor connecting all thin film experiments to date is epitaxy on (001) MgO. It is important to know if and how this specific substrate/film relationship influences the lattice constant trends. To address this question, composition J35 (J14+Cr) was grown on (100) MgO, (100) MgAl$_2$O$_4$ (Spinel), (0001) sapphire. These substrates were chosen because they offer similar epitaxial registry (spinel) but with much larger lattice mismatch, and a different crystallographic orientation (sapphire) accompanied by substantially larger mismatch. In addition, composition J14 was prepared on ceramic alumina to explore the situation of random interfacial registry. For all depositions an MgO substrate was included simultaneously as an internal control to assure that the trend is reproducible. MgAl$_2$O$_4$ has a lattice parameter of 8.08 Å (for the 8 FCC oxygen sublattice unit cell) [141], therefore a lattice mismatch of approximately 4.3% for cube-on-cube growth, and thus a relaxed film. For cubic systems on basal plane sapphire <111> oriented growth is expected[142], [143]. As in the previous section, films were prepared as a function of substrate temperature and lattice constants were recorded, Figure 6.5 shows the representative scans of J35 on (0001) sapphire and (100) spinel from 200 °C to 500 °C in 50 °C increments under a constant O$_2$ pressure of 50 mTorr. Two details become evident: 1) the main (111) peak shown in the top image shifts to the right as temperature increases, and 2) phase separation into rocksalt plus spinel occurs, as evidenced by the appearance of (111) and (511) spinel peaks at 450 °C. A similar trend is seen in the (200) J35 peaks on MgAl$_2$O$_4$ where phase separation appears around 500 °C.
Figure 6.5 J35 series grown on (0001) sapphire and (100) spinel substrates at incremental temperatures from 200 °C - 500 °C at 50 mTorr pO2. Phase separation occurs at 450 °C. The in-plane relationship of J35 grown on sapphire is shown in supplemental Figure 6.24.
To understand lattice constant and phase stability trends in J35 under these specific growth conditions, we focus on the 200 °C-400 °C temperature range. Figure 6.6 (a-c) show a blow up of the two-theta range for the (002) reflection for each substrate. In each case the out-of-plane lattice parameter shifts to higher 2θ values with increasing deposition temperature. The corresponding change in inter-planar spacing is summarized in Figure 6.7; the previous trend exists regardless of substrate, however the total shift from the metastable unit cell dimensions is different for different substrates.

Figure 6.6 Composition J35 grown on a) MgO, b) c-sapphire, and c) Spinel in 50 °C increments from 200 °C–400 °C at 50 mTorr pO2. In all cases the same lattice trend exists, regardless of substrate.
These unexpected trends warranted a similar deposition temperature trend experiment for the parent composition J14. The results are shown in Figure 6.8 and reveal yet another temperature dependent behavior. Between 200 °C and 350 °C, the out-of-plane lattice parameter is smaller than the bulk value and remains relatively constant at 4.18 Å. From 400 °C to 700 °C, the out-of-plane lattice parameter shifts discretely to lower 2θ, corresponding to a consistent lattice parameter of 4.28 Å. J14 prepared at 375 °C exhibits the diffraction pattern in Figure 6.9 XRD diffraction pattern around the a) 200 MgO peak depicting complex interference which limits the accuracy of lattice parameter calculation b) the 204 skew-symmetric reflection enabling calculation of lattice
parameter, $c = 4.207 \text{Å}$. (a). While this pattern is difficult to interpret due to complex interference between the film and substrate diffracted intensities, it appears cubic with a lattice constant of 4.20 Å, which is close to the bulk MgO value of 4.21 Å [144].

![Lattice distortion as a function of deposition temperature for J14 host: a) diffraction series and b) corresponding lattice parameter vs. temperature. From 200 °C-350 °C, $c$ remains constantly smaller than the substrate. At 400 °C and higher, $c$ becomes larger than the substrate.](image-url)

**Figure 6.8** Lattice distortion as a function of deposition temperature for J14 host: a) diffraction series and b) corresponding lattice parameter vs. temperature. From 200 °C-350 °C, $c$ remains constantly smaller than the substrate. At 400 °C and higher, $c$ becomes larger than the substrate.
Figure 6.9 XRD diffraction pattern around the a) 200 MgO peak depicting complex interference which limits the accuracy of lattice parameter calculation b) the 204 skew-symmetric reflection enabling calculation of lattice parameter, $c = 4.207\text{Å}$. 
As a reference, in addition to growth on MgO, J14 was grown on a polycrystalline alumina substrate at 500 °C under 50 mTorr O₂. Figure 6.10 J14 film grown on a polycrystalline alumina substrate resulting in a polycrystalline film with calculated lattice parameter consistent with the bulk value for cubic symmetry. Contains XRD results indicating polycrystalline film growth with lattice parameters consistent with bulk J14.

This result is particularly interesting because it suggests that extended lattice constants are related to either epitaxial growth or a film structure featuring a crystallographic orientation. At this stage we cannot discern which one, if either, provides the predominant influence.
From the above experiments, it is clear that laser ablation deposition can enhance the effective stability of multicomponent thin films especially concerning additional cations with “high contrast” in radius or valence. It is also clear, though not understood, that deposition conditions, in particular temperature, can modify the film structure in dramatic fashion. The stability of these structures in response to post-deposition heat treatments invites exploration. To begin this process we select a film of composition J30 deposited at a substrate temperature of 350 °C. J30 is the best candidate given the large magnitude of lattice constant variation that is possible and the stability of Sc in the 3⁺ valence state. The sample was annealed after deposition in air at 700 °C for 1 hour. We know from previous measurements that J30 will transition toward a cubic structure by relaxing the out of plane lattice parameter upon deposition at 700 °C, but we do not know if phase purity is retained. To do so, we conducted x-ray scans before and after annealing, the result of which are shown in Figure 6.11.
Figure 6.11 XRD scan of before and after post deposition anneal of J30 grown at 350 °C.

These x-ray scans illustrate that upon annealing, the initially non-cubic structure “relaxes” back to cubic with a new lattice constant similar to bulk composition J14, and a second phase nucleates. While we do not know the second phase composition, and from this scan alone we cannot discern the structure, we presume it to be scandium-rich. What is ultimately important about this result is the connection between the solubility of component six and the temperature dependent structural distortion. The data suggests that the tetragonal distortion is associated with Sc accommodation.
There are many additional experiments needed to understand these stability limits that are beyond the scope of this thesis. The most important include:

- What is the role of epitaxy and does the lattice mismatch influence the stability range?
- Does upper stability limit depend upon the deposition temperature?
- How does the stability limit depend on the properties of component six?

6.4.3 Pressure Study of J35 thin films grown on MgO

From the data above we appreciate the impact of both temperature and substrate on the structure and stability of six-component oxides, which we speculate are possible to observe because they are frozen in an extreme-quenched state. This hypothesis can be tested by preparing similar compositions as a function of deposition pressure where the “extremeness” of the quenching is tailored. To do so, we select the candidate J35 prepared over the same temperature range as in the original experiment, except this time the O$_2$ is varied between 50 mTorr to 10mTorr. In principle, lowering the pressure should reduce gas phase scattering thus adding more kinetic energy to adatoms arriving at the film surface. The lattice constants were determined for the entire set by diffraction and the temperature dependent data are shown in Figure 6.12(a). In summary, the lattice constants are reduced by approximately 5% and the phase stability region shifts to a temperature range between 300 °C to 500 °C (fig. 6.10(b)). Additional x-ray scans show that above 600 °C the samples phase separate into a rocksalt and a spinel, these scans are shown in supplementary Figure 6.23.

These experiments suggest that the out-of-plane lattice effect is somehow related to the amount of oxygen present during growth, or the energetic bombardment, or a combination of both. If this suggestion holds true, depositing another temperature series
at an intermediate O$_2$ pressure should yield an overall lattice parameter shift that is also intermediate. A second temperature series was grown under a constant O$_2$ pressure of 30mTorr. Figure 6.13 shows the individual x-ray patterns and the extracted lattice constant data for J35. The stability region for single-phase material now spans from 300 °C - 450 °C. The summary of all lattice constant data, including the reference 50 mTorr deposition pressure is given in Figure 6.14. Generally speaking, the trend of decreasing out of plane lattice constant with increasing temperature is present for all pressures, the magnitude of the lattice constant increase is larger for lower pressures, and the temperature range over which the single-phase state can be stabilized increases with lower pressure.
Figure 6.12 Diffraction series (a) of J35 grown at 10 mTorr pO2 from 250 °C–700 °C with corresponding lattice parameters and inferred instability regions (b).
Figure 6.13 Diffraction series (a) of J35 grown at 30 mTorr pO2 from 300 °C - 500 °C with corresponding lattice parameters and inferred instability regions (b).
Figure 6.14 Scatter plot of $c$ versus deposition temperature for J35 grown on MgO under 10, 30 and 50 mTorr $O_2$. Instability regions shift with temperature and $O_2$ pressure, as evidenced by the appearance of (111) spinel peaks shown in supplementary Figure 6.23 Diffraction patterns showing the temperature and pressure dependent development of a (111) spinel peak in composition J35 indicating phase separation into a rocksalt + spinel for a) 10 mTorr $O_2$, b) 30 mTorr $O_2$, and c) 50 mTorr $O_2$. 
To further explore this pressure trend, another J35 series was grown at a constant temperature of 300 °C and O₂ pressures of 10, 20, 30, 40, and 50 mTorr, the diffraction data are shown in Figure 6.15. Here one can appreciate the exponential relationship between the out-of-plane lattice parameter and deposition pressure.

![Diffraction Series](image)

*Figure 6.15 Diffraction series of J35 grown at a) 300 °C in 10 – 50 mTorr O₂ with b) the corresponding exponential change in out-of-plane lattice constant versus O₂.*

To this point, the lattice parameter trends are highly dependent on deposition temperature as well as O₂ pressure. It is interesting to note that a decrease in crystal quality appears to accompany the lowest deposition pressures. The x-ray patterns for thin films prepared at 10 mTorr show the broadest peaks and weakest fringing. Most likely, bombardment at these low pressures is now damaging the subsurface of the growing film.
To further investigate contributions from bombardment, we conducted an additional pressure series using Ar/O2 mixtures. For each deposition, the total pressure inside the deposition chamber was held constant at 50 mTorr, but the gas mixture was varied such that the oxygen content spanned 10 mTorr to 50 mTorr. In so doing, the gas phase scattering for each deposition should be similar, but the oxygen activity will vary. The lattice constant data for this series is shown in Fig 6.16 along with the data for pure oxygen, these data were collected at 300 °C. These data show that lattice constants increase with decreasing total pressure O2 and with decreasing O2 partial pressure. The rate of increase is similar in each data set, with the exception of the lowest pressure. This result suggests that lattice constant increases are associated with more reducing conditions and that bombardment may have a less important role in lattice constant modulations.
Figure 6.16 Plot of c-lattice constant versus oxygen pressure for total pressure and partial pressure series. Regardless of the trend function, both systems experience a decrease in lattice parameter with increasing oxygen content.

Similarly, two additional deposition sets were made as a function of deposition temperature with different Ar:O2 ratios totaling 50mTorr to compare to the 10 mTorr and 30 mTorr O2 experiments. In figure 6.17(a) we compare directly films prepared at a total pressure of 10 mTorr O2 with those prepared at 50 mTorr 80:20 Ar:O2, while In figure 6.17(b) we compare directly films prepared at a total pressure of 30 mTorr O2 with those prepared at 50 mTorr 40:60 Ar:O2. In both cases, lower deposition temperatures favor larger lattice constants.
Based on this set of x-ray data, we hypothesize that cation oxidation states are systematically changing within the film in response to a more reducing deposition environment. We note that both higher temperatures and lower oxygen pressures shift the deposition to more reducing conditions. Additionally, the transition from rocksalt to spinel shifts to a higher temperature when the pO$_2$ is lower, thus increasing the stability window of the entropy-stabilized phase. At this stage, additional experiments are needed to comment on the origins of this trend.

As a final experiment we performed post deposition anneals on several samples prepared at different growth parameters, the intent being to test if the “relaxed” state depended upon the prepared state. Films with the J14 and J30 compositions were used. In all cases they were annealed at 700 °C in air for one hour. Figure 6.18 shows the lattice parameters of film samples from (a) J14 and (b) J30 plotted before and after annealing. The results show each film relaxes back to the same respective lattice constant regardless or original growth parameters and lattice constant. While this does not explain the origins of lattice constant changes, it supports the hypothesis that oxidation state is playing a role in the observed trends, and that annealing returns each system to its respective equilibrium oxidation state. To a reasonable approximation, cation stoichiometry will not change after a 700 °C anneal in air, but oxygen ingress and egress can be altered substantially.
Figure 6.17 Plots of $c$ versus deposition temperature for a) the 10mTorr $O_2$ series and b) the 10mTorr $O_2$ series. Again, while there is a slight shift in overall lattice parameter between the pure $O_2$ and the $pO_2$ series, the overall trend of decreasing lattice constant as temperature increases remain the same.
The observed trends in J35 invoke questions regarding whether the differing lattice parameter trends are unique to six component ESO-type systems. As a step towards an answer, a parallel experiment of similar parameters was done on a two-component system containing Mg and Ni. MgO and NiO are both components in ESO prototype J14 and therefore exist in J35 as well as the other compositions mentioned earlier; they also exhibit complete solid solubility [145]. Mg is an isovalent cation with a 2+ oxidation state, while Ni is a transition metal cation that can exhibit 1+, 2+, 3+, or 4+ depending on its surrounding complex [146]–[148]. The most thermodynamically stable state for Ni,
however, is $2^+$ in rocksalt form. If the hypothesis that changes in cation oxidation state play a critical role in lattice parameter changes, it should hold that doing a temperature study on an isovalent system results in negligible effects.

A series of thin films were grown on (100) MgO substrates at 50 mTorr O$_2$ using three compositions: Mg$_{0.99}$Ni$_{0.01}$O, Mg$_{0.50}$Ni$_{0.50}$O, and NiO; each at 400 °C, 500 °C, and 600 °C. The rationale is as follows: NiO has 100% cations with “flexible” valence state, 50/50 NiO/MgO has 50% cations with “flexible” valence state, and 1/99 NiO/MgO has 1% cations with “flexible” valence state. The 1% is necessary to change the lattice constant so avoid complete overlap with the substrate. If flexible valence cations are a necessary component of lattice constant changes, their magnitude should depend on Ni content. The XRD results, illustrated in Figure 6.19 show a growing trend as a function of Ni content. Mg$_{0.99}$Ni$_{0.01}$O exhibits negligible variations in 2θ, while Mg$_{0.50}$Ni$_{0.50}$O and NiO shift to lower 2θ as temperature increases by a total of 0.25% and 0.48%, respectively. The corresponding lattice parameters are plotted in Figure 6.20.

For reference, NiO has a smaller lattice constant than MgO by ~1.25%. Thus, one expects biaxial tension on the larger MgO template and perpendicular (out of plane) compression. Experimentally, we find that at 600 °C, the observed out of plane lattice constant is close to the expected bulk value for all cases. As the deposition temperature decreases, the out of plane constant increases substantially. This trend cannot be explained by epitaxial strain as this would predict an opposite trend and under the present range, temperature should not affect it. Annealing these films results in a relaxation toward the expected bulk lattice constants based on Vegard’s law approximations, as shown in Figure 6.21.

At this stage, it is ill-advised to speculate on specific origins of lattice constant changes in these materials. However, the set of experiments, particularly the NiO-MgO films,
suggest that deviations in oxidation state among those cations that can exhibit several appear to be an important contributor.

Figure 6.19 XRD series depicting the change in out-of-plane lattice parameter for composition \( \text{Mg}_{1-x} \text{Ni}_x \text{O} \) with a) \( X = 0.01 \), b) \( X = 0.5 \), and c) \( X = 1 \). Films are commensurate to the substrate. Vegard’s law predicts bulk lattice parameters for a) 4.212Å and b) 4.187Å. The lattice parameter used for NiO bulk is 4.16Å.
Figure 6.20 Scatter plot of c versus deposition temperature.
In these initial studies we recognize the existing lattice constant trends are dependent on substrate temperature, sixth component species and deposition pressure. Growth of J35 on MgO, spinel, and c-sapphire concludes that while the metastable lattice constant varies per substrate, the overall trend remains consistent. J14 maintains a lattice constant trend unique in that it exhibits a discrete shift from compressive to tensile values. Further, depositing J14 on polycrystalline alumina at 500°C shows no indication of lattice parameters comparable to those found when J14 is deposited on MgO. This
suggests that the lattice constant trend is related to either epitaxial or textured growth. At this time we do not know the nature of this relationship, or which mechanism is predominate. In addition to the lattice parameter trends observed in J35, it is found that a secondary spinel phase occurs at higher temperatures. Lowering the oxygen pressure during deposition shifts lattice constants to higher values and increases the temperature at which spinel appears. This provides a wider stabilization window and suggests oxidation state may play a role in observed trends. Annealing these films post deposition results in a lattice relaxation to the same constant values regardless of original deposition parameters furthering our suspicions concerning cation oxidation state. The NiO-MgO study proves consistent with our hypothesis in that the shifts in lattice constant are noticeable related to the amount of “valence-flexible” Ni in the films. However, the relationship between lattice trends and oxidation state is complicated more by the fact that these compositions contain multiple “valence-flexible” cations capable of a multitude of oxidation states. Ultimately, this work stands incomplete. While we hypothesize that valence changes are responsible for lattice parameter trends, other possibilities could play a minor role including vacancies and concentration gradients. There are many questions that need answered and experiments devised in order to rigorously understand the underlying mechanisms governing these ESO thin films.

6.5 Conclusions

This study explores possible explanations for the observed lattice constant changes in additional ESO based compositions. Compositions containing Sc, Sb, Sn and Ge increase in c-lattice constant as temperature increases while Cr decreases. Using the Cr composition as a test subject, growth on differing substrates appears to have a negligible effect on lattice parameter trends. Oxygen pressure studies suggest that oxygen plays a crucial role in the observed trends, as decreasing O\textsubscript{2} shifts the overall
trend to lower $\theta$ and increases the transition point from a rocksalt structure to a rocksalt+spinel. Annealing these films results in a relaxation to a common equilibrium position based on composition, consistent with previous work in the literature that suggests a change in oxygen content, altering cation valence. Observed trends in the ternary Mg-Ni-O compositions provide a self-consistency with the valence hypothesis. It is possible that ion bombardment has a slight effect on the growth of the six-component systems, however, like most of this work, it requires a more in-depth study to come to a solid conclusion.

6.6 Acknowledgements

CMR and JPM would like to acknowledge Dr. David Harris for his initial work on the J30 series that inspired the bulk of this investigation. Acknowledgement also goes to GyungHyung Ryu, who spent a summer with us growing thin film samples.
6.7 Supplementary Data

Figure 6.22 Example of an off-axis XRD series for (left) composition J31 and (right) composition J35. In-plane lattice parameters are calculated by fitting these film peaks in conjunction with the (002) film peaks.
Figure 6.23: Diffraction patterns showing the temperature and pressure dependent development of a (111) spinel peak in composition J35 indicating phase separation into a rocksalt + spinel for a) 10mTorr $O_2$, b) 30mTorr $O_2$, and c) 50mTorr $O_2$. 
Figure 6.24 $\phi$-scan of J35 grown on c-sapphire. The (104) sapphire planes exhibit three-fold symmetry along <0001>, while J35 exhibits three-fold symmetry along <111> with two directional domains oriented $\pm 30^\circ$ to the substrate.
7 Conclusions and Future Work

7.1 Conclusions

Entropy-stabilized oxides are a novel class of materials that capitalize on configurational entropy to promote single phase formation and stability. Through a series of thought experiments and basic knowledge of thermodynamics, four testable criteria were developed to determine genuine entropic stabilization.

1. The phase transition from multiphase to single phase must be reversible through the transition temperature, similar to a eutectoid.
2. Lowering the configurational entropy by removing any given component from the composition should destabilize the phase.
3. Manipulating the amount of one component such that equimolarity between constituents no longer holds true should result in phase destabilization at the equimolar transition temperature. As configurational entropy is systematically decreased, the transition temperature at which single phase occurs should correspondingly increase.
4. The phase transformation from multiphase to single phase should be endothermic, demonstrating that enthalpy did not play any role promoting phase stabilization.

Using a compositional prototype called J14, Mg$_{0.2}$Co$_{0.2}$Ni$_{0.2}$Cu$_{0.2}$Zn$_{0.2}$O, each of these four criteria were experimentally tested using solid state synthesis methods, high temperature annealing cycles, powder x-ray diffraction (PXRD), and differential scanning calorimetry (DSC). Results found this composition to be truly entropy stabilized. It was further confirmed using scanning transmission electron microscopy (STEM), electron dispersive spectroscopy (EDS), and extended x-ray absorption fine structure (EXAFS) that J14 was a rocksalt solid solution, with no evidence of local
cation clustering, indicating configurational entropy is at a true maximum and little to no enthalpy-driven correlation preference is present.

Through EXAFS it was also confirmed that there exists local structural disorder within each cation coordination complex of bulk J14, corresponding to differences in cationic radii. Co, Ni, and Zn absorbers shared a similar local structure where octahedral bond lengths are slightly smaller than estimated by the Shannon radii. Cu octahedra exhibit distortions consistent with Jahn-Teller effects. Mg was not measured due to the energy range limits of the beamline but was estimated based on the MgO lattice constant. Local distortions appear to average out by the next nearest neighbor coordination shell, with a scattering path length consistent with J14 lattice parameters determined through Rietveld refinement. All clustering models resulted in poor fit metrics indicating the likelihood of a random cation distribution at the smallest length scales.

Three compositions tested the hypothesis that higher temperatures and non-equilibrium conditions could increase probability of phase stabilization. Pulsed laser deposition (PLD) was used as a medium to increase the effective temperature of ESO synthesis through the high energy kinetics associated with ablation. The first composition, denoted T22, formed a two phase system consisting of mixed spinels. PLD on a native Si substrate resulted in the commensurate growth of a single phase rocksalt system with a lattice parameter consistent with Vegard’s Law. The second and third compositions tested the solubility limitations of the ESO prototype through strain and valence misfit, respectively. Under bulk synthesis, ScO$_{1.5}$ was found to be almost completely immiscible with J14 based on x-ray diffraction analysis (denoted J30). PLD on native Si substrates resulted in a textured film consistent with rocksalt but could not be confirmed due to a random in-plane orientation. Growth on an MgO substrate yielded a single crystal epitaxial thin film consisting of rocksalt. Similarly, the addition of CaO to J14 (J14C) resulted in multiple rocksalt phases as well as the dissolution of CuO tenorite from the J14 host. PLD on MgO resulted in a relaxed film consisting of a single
phase rocksalt structure with a lattice parameter consistent for containing 20% Ca
cations. These films were re-characterized periodically using XRD. As no changes
presented in recent diffraction patterns, it was concluded that these systems are
substantially metastable.

The epitaxial growth of J30 inspired a series of compositions containing sixth elements
including Cr (J35), Sb (J31), Sn (J34), and Ge (J36). Each of these six component
systems exhibits a systematic change in out-of-plane lattice constant as a function of
deposition temperature. Growth of J35 on MgO, MgAl$_2$O$_4$, and c-Sapphire found no
substrate influence on said trend. Variations in pO$_2$ while holding temperature constant
during deposition resulted in an overall shift in the lattice constant series, suggesting
either bombardment or oxygen content as a possible cause. Lowering the O$_2$ shifted the
rocksalt to spinel transition temperature higher, consistent with a change in the
oxidation threshold. Any post annealing of these thin films causes relaxation to the
same lattice parameter regardless of as-deposited lattice constant, suggesting oxygen
to have a specific role in these materials.

7.2 Future Work

Collectively, ESO materials have the potential to exhibit new and exciting structure-
property relationships based on their configurational disorder. While this work is minute
in comparison to efforts placed in other materials systems such as high entropy alloys, it
must be realized that these studies completely new. That being said, there are many
avenues for continued, more in-depth explorations of not only the basic theory behind
bulk and thin film ESOs but also properties and applications. Below is a small list of
potential avenues for further exploration.

- One of the primary causes of epitaxy disruption in thin film growth on Si is the
formation of the disordered surface reaction with oxygen, SiO$_2$. As a method to
overcome this issue, Si substrate surfaces are often cleaned and passivated though an HF/ethanol treatment [149], [150]. In chapter 5, composition T22 was deposited on an untreated (100) Si substrate resulting in an epitaxial relationship found to be <100>T22 || <100>Si. φ-scans show an in-plane alignment consistent with four unit cells of T22 matching 3 unit cells of Si with a mismatch of only ~0.5%. Based on this information, there may be a reaction taking place between the T22 and SiO2 interface that results in unconventional epitaxial growth. The interface and the mechanisms driving its formation should be further investigated to advance knowledge in epitaxial interface engineering.

- EXAFS has shown to be an effective tool for investigating the local structure of bulk ESOs. In chapter six, the ESO concept is expanded to thin film growth resulting in several new compositions that exhibit interesting size variations hypothesized to be the result of competing oxidation states between cations. Through XAFS, the combination of EXAFS and XANES, we will be able to observe local structural changes around absorbing atoms of interest and correlate them to changes in oxidation state between atoms. This work has been initiated on compositions J14, J31 and J35, where EXAFS data was collected for the Cu absorber at APS beamline 10-BM. However, due to time constraints and lack of additional structural information, the proper theoretical model has not yet been developed. Obtaining more structural information on these compositions will enable development of a more confident model, and XANES work will provide complimentary information on changing valence states.

- Li-ion battery research is currently trending due to high energy densities and overall low self-discharge rates. A major source of difficulty lies in the structural degradation of cathode materials after so many charge/discharge cycles [151]–[153]. ESO materials could be substituted for common cathode materials, such
as LiCoO$_2$, with the intent to better stabilize the structure though high configurational entropy. Work is currently underway as we have combined one of our ESO compositions, C2 (see appendix A), with Li to form the rhombohedral structure Li[C2]O$_2$. Preliminary results find minimal redox activity compared to LiCoO$_2$, which may be caused by choosing cations with few possible oxidation states. Proper cation substitution into C2 should improve the redox activity and lead the way to future testing of cycling stability.
References


Appendix A  Compositions

The following table is a list of attempted compositions and their phases after reaction in air at 1000 °C for 24 hours. This list is not all inclusive.

Table A.1 Compositions

<table>
<thead>
<tr>
<th>Name</th>
<th>Components</th>
<th>Bulk Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>CuO, MgO, Fe2O3, ZnO, TiO2</td>
<td>Single Phase</td>
</tr>
<tr>
<td>T2</td>
<td>MgO, TiO2, ZrO2, Fe2O3, Al2O3</td>
<td>Multiphase</td>
</tr>
<tr>
<td>T3</td>
<td>NiO, MgO, Al2O3, ZnO, TiO2</td>
<td>Multiphase</td>
</tr>
<tr>
<td>T4</td>
<td>CuO, MgO, Fe2O3, ZnO, ZrO2</td>
<td>Multiphase</td>
</tr>
<tr>
<td>T5</td>
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<td>Multiphase</td>
</tr>
<tr>
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<td>J11</td>
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<td>MgO, NiO, Mn, ZnO, CoO</td>
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</tr>
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</tr>
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</table>
Appendix B  EXAFS

Extended X-Ray Absorption Fine Structure (EXAFS) played a significant role in understanding the local structure of ESOs. This appendix is written as a basic and practical guide to EXAFS theory, measurement, and analysis. For a more in-depth, yet understandable, guide to EXAFS (and XANES) reference [99] is highly recommended.

B.1 Theory and Explanation

EXAFS is a characterization technique that uses high intensity x-rays to probe the local structural environment around a particular elemental species. Synchrotron light is cycled into the beamline from the storage ring and passed through a monochromator, focusing slits and finally incident upon a sample, as shown in Figure B.1.

![Simplified schematic of a XAFS beamline](image)

*Figure B.1 Simplified schematic of a XAFS beamline. The most common (and perhaps most stable) measurement mode is transmission. If the samples do not meet the thickness criteria or contain a dilute species, a fluorescence detector may be a good alternative. Electron-yield is also a measurement mode for XAFS, but avoided entirely because it is never used in this work.*
As with any typical absorption experiment, the data analyzed is absorption coefficient, \( \mu \), versus energy, \( E \). The absorption coefficient can be found through the Beer-Lambert relation:

\[
I = I_0 e^{-\mu x}
\]

where \( I \) is post-absorption intensity, \( I_0 \) is the pre-absorption intensity, and \( x \) is the thickness of the sample. The monochromator scans through energy space around a known elemental absorption edge, such as Cu K1, and upon absorption a steep increase in \( \mu \) is observed. The magnitude of energy absorbed corresponds to the binding energy of a core electron, releasing it from the atom resulting in spherical wave propagation throughout the sample (crystalline or amorphous). The wave backscatters from neighboring atoms, interfering either constructively or destructively with itself. This process is depicted in Figure B.2. Said interference gives rise to an oscillatory pattern at energies above the absorption edge, known as the EXAFS, shown in Figure B.3.

![Diagram of absorption and emission process](image)

*Figure B.2 The absorption and emission process. When x-rays are incident upon an elemental species with a core electron binding energy comparable with that of the light wave, a photoelectron is emitted in the form of a spherical wave. As the wave expands outward, it scatters from neighboring atoms. The interference between the forward and back scattering wave functions give rise to the EXAFS.*
Subtracting the absorption edge from the $\chi_{\mu}(E)$ spectra and plotting as a function of k-space where

$$k = \frac{2\pi}{h} \sqrt{2m_e (E - E_0)}$$

isolates the EXAFS, which is generally described by the equation

$$\chi(k) = S_0^2 \sum_i N_i \frac{f_i(k)}{kR_i^2} e^{\frac{-2R_i}{\lambda(k)}} e^{-2k^2\sigma_i^2} \sin[2kR_i + \delta_i(k)].$$

In (B.2), $h$ is Planck's constant ($4.136 \times 10^{-15}$ eV·s), $m_e$ is the mass of an electron ($9.10938356 \times 10^{-31}$ kg), $E_0$ is the binding energy of the emitted core electron, and $E$ is the energy of the incident photon.

In (B.3), $S_0$ is the scattering amplitude, $f_i(k)$ is the amplitude of the $i$th shell, $N_i$ is the number of neighbors at the $i$th shell, $R_i$ is the distance to the $i$th shell, $\sigma_i$ is the Debye-Waller factor, and $\lambda(k)$ is the mean free path.
Figure B.3 Typical XAFS measurement before processing. The energy range spans 200eV below the known absorption edge of an element (pre-edge) to 800-1200eV above the edge depending on signal-to-noise ratio and whether there is another edge. The XANES region (not analyzed in this work) is approximately -30eV to 50eV around the absorption edge. Above 50eV is considered the EXAFS region.
The variables and functions in the EXAFS equation (A.3) can be defined as follows in Table B.1.

**Table B.1 Definitions of EXAFS equation terms.**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0^2$</td>
<td>Amplitude Reduction Factor</td>
<td>Constant compensating for the fact that the absorbing atom is no longer the same after losing a core electron.</td>
</tr>
<tr>
<td>$N_i$</td>
<td>Degeneracy</td>
<td>Multiplicity factor for the same elements at the same average distance from the absorber. In single scattering events, this is the number of atoms in a particular coordination shell.</td>
</tr>
<tr>
<td>$f_i(k)$</td>
<td>Scattering Probability</td>
<td>Analog to the elemental scattering factor in XRD.</td>
</tr>
<tr>
<td>$R_i$</td>
<td>Half Path Length</td>
<td>Half the length of scattering path, i.e., total path is defined as the entire distance from the absorber, to the scatterer, and back. For a single scattering event to a nearest neighbor, the bond length is equal to one-half the scattering path length.</td>
</tr>
<tr>
<td>$\lambda(k)$</td>
<td>Electron Mean Free Path</td>
<td>k-dependent mean free path of the photoelectron.</td>
</tr>
<tr>
<td>$\sigma_i^2$</td>
<td>Mean-Square Relative Displacement</td>
<td>The square of the standard deviation of half path length. Can account for both variations in bond length of particular coordination shell as well as thermal displacements. Also called the “EXAFS Debye-Waller Factor”.</td>
</tr>
<tr>
<td>$\delta_i(k)$</td>
<td>Phase Shift</td>
<td>Accounts for phase shifts of the spherical wave from changes in local potential as well as scattering events.</td>
</tr>
</tbody>
</table>

Using the EXAFS equation, information on the average local structure around a particular absorbing species is obtained. This includes neighboring species, coordination number, and bond lengths. There are several ways to extract this information from an EXAFS spectrum including Principal Component Analysis, Linear
Combination Analysis, and Fingerprinting. However, due to the fundamentally complicated nature of ESOs, the primary analysis technique used in this work is through theoretical modeling. The following two sections serve as a commentary for ESO data reduction and analysis using a theoretical standard. They are by no means complete, but they provide some insight into handling ESOs versus another type of system.

**B.2 Data Processing**

Data processing is done using Athena, a program in the Demeter 0.9.20 software suite (open source software) by Bruce Ravel [103]. The following is an example data reduction for EXAFS above the Ni K-edge at 8333eV in a J14 powder sample collected at APS 12-BM. Keep in mind that not all beamlines are created equal, so there will be modifications to data reduction depending on chosen line and/or beam fluctuations. This section covers the very basics of data reduction, so many of the functional capabilities of Athena will not be mentioned in this text.

Typically, one takes several repeat scans of the same sample in case of beam fluctuations or detector glitches. Importing all scans from the J14_Ni series shows three scans superimposed on one other. In addition to the sample scans, three simultaneous reference scans are measured using a metal foil (in this case, Ni). Figure B.4 Raw data graphs of three consecutive XAFS measurements of the Ni absorber in J14 shows the sample spectra for the three samples scans around the Ni absorber. The first absorption edge corresponds to Ni, while the second edge at 8979eV corresponds to Cu. Seeing another absorption edge may be common in many ESO systems considering the constituent species are closely spaced on the periodic table. Truncate the spectra around 50eV below the second absorption edge.
The next step in data reduction is to calibrate the absorption edges in energy space. If a reference scan was measured simultaneously, it is automatically linked to a corresponding sample measurement in Athena. Therefore, anytime a reference spectrum is shifted in energy space, the corresponding sample spectra will shift the same amount. There are many places to choose absorption edge energy, $E_0$, the preference is up to the PI. It can be anywhere along the edge, however, one must always stay consistent! With a particular scan selected go to the calibration menu. Use the first derivative to pick the very first peak in the spectra, then go to the second derivative and “find zero point”. The number output is where $E$ will become $E_0$. The same is done for the reference spectra. Once the reference spectra are marked correctly, press “calibrate”, and all spectra will shift to their calibrated position. Since the reference is a metal foil, its edge should begin a few eV below that of the Ni in J14†.
Figure B.5 First derivative of a J14-Ni spectrum. The absorption edge should be marked as the first peak regardless of how intense it may be.
Figure B.6 First derivative of the Ni foil spectra. Again, the first peak is chosen to maintain consistency. The intensity of this peak versus the one of J14-Ni is due to the severity of the slope at the onset of the absorption edge.

Occasionally the monochromator will “glitch” due to either picking up a diffraction peak or for some other reason. This manifests itself in the $\chi(k)$ spectrum as sharp peaks that do not fit the oscillatory trend as shown in Figure B.7. These can be removed in the deglitching menu. Once all scans are properly aligned, truncated, and deglitched, the sample scans can be merged into a single spectrum. Do not mark the reference scans, they will merge automatically. The merged spectrum of J14-Ni is shown in Figure B.9.
Figure B.7 $\chi(k)$ spectrum showing glitches, denoted by arrows.
Figure B.8 Collective $\chi(k)$ spectra for all J14-Ni runs after glitch removal.
Figure B.9 Merged $\chi(k)$ spectrum containing all J14-Ni runs. Notice the signal to noise improvement over the individual scans.

Now that the scans are merged, normalize the $\mu(E)$ curve by fitting a pre-edge and post-edge polynomial function, respectively. Normalization will happen automatically once “Normalized” is selected in the plot menu located in the bottom-right corner. This fits the spectra to oscillate around 1, as shown in Figure B.11.
Figure B.10 Pre and post-edge fitting for $\mu(E)$ normalization.
Figure B.11 Normalized $\mu(E)$.

Perhaps the trickiest part of EXAFS isolation is the background subtraction. The background subtraction removes any of the low frequency oscillations from the EXAFS region (50-100eV above the edge), and choosing too high a value could result in removing viable information. A rule of thumb is to set the RBKG value to one half the closest scattering path. Usually the preset value of 1 that Athena chooses is acceptable, so do not focus too much on this step.
The final step in data reduction is choosing an appropriate k-range for the Fourier transform. In general, the range should be such that they land on nodes (where the $\chi(k)$ function equals zero, and $k_{\text{min}}$ should be sufficiently far from zero to avoid any remaining effects from the XANES region. If data is too noisy at higher $k$, then $k_{\text{max}}$ should be picked before such noise is significant. For this example, we choose the k-range to be from 3.423-11.578. Pressing the "R" button takes the transform of $\chi(k)$ within the designated range, as shown in Figure B.14. At this point the prepared data should be saved as an Athena project and we can move on to modeling.
Figure B.13 Chosen range in $\chi(k)$ for Fourier transform and analysis.
Figure B.14 Resulting Fourier transform of the $\chi(k)$ spectrum. Most commonly used for model fitting.
B.3 Data Fitting Using a Theoretical Standard

EXAFS is by no means a black box characterization technique. In order to be effective in data collection and analysis one must know what questions need an answer. In the case of ESO systems, our intent is to understand the local structure of individual coordination complexes and the degree of cation disorder within the neighboring cation coordination shell. To even begin the modeling process we need to have a reasonable idea of the structure we are analyzing. Through other, more readily accessed characterization techniques such as x-ray diffraction and TEM, we already know we are working with a cubic rocksalt system with a lattice parameter of ~4.23Å. There are no indications of peak splitting or superlattice-like ordering, thus our first idea of the structure is a single phase rocksalt solid solution.

Modeling and data fitting are done using Artemis, another program in the Demeter XAFS suit. The basic steps for data modeling are as follows:

1. Add the data set of interest. In this case it is the reduced spectrum from the J14 Ni absorber.

2. Add a Feff calculation. Here you will be prompted to open an "Atoms" file, which is a file containing crystallographic data like one would find in CrystalMaker. Chances are you do not have one, so right click the “Add” button and select a blank template. In the Atoms tab shown in Figure B.15, input your known crystallographic information; lattice constants, symmetry, and elements. *IMPORTANT: Atoms does not allow you to have partial occupancy in the elements table. So it is best to build five different rocksalt FEFF calculations for the five different cations in the composition. Choose the cation to be the core. Once this tab is filled, press “Run Atoms”. The output opens under the Feff tab, with a list of lattice positions and potentials that depend on the atomic number of
the species listed in the first tab. This text can be manipulated. Under the “POTENTIALS” section, make sure the ipot = 0 elements correspond to the specific absorber of your data! This is highlighted in Figure B.16. Otherwise your fit will be frustratingly wrong. What this particular example essentially tells Feff is that you have a crystal structure with one absorbing atom, Ni, and it exists in a ZnO rocksalt matrix. The scattering paths generated will be from the Ni absorber, to a scattering element, and back. Pressing Feff will run the potentials and scattering probabilities within the crystal and output a list of individual scattering paths, shown in Figure B.17. Repeat this process for every cation in the ESO system such that there are five Feff calculations modeling a single absorber within another species’ cation matrix.
Figure B.15 Screenshot of Atoms tab in Artemis showing crystallographic input information.
Figure B.16 Screenshot of Feff output tab in Artemis, providing the calculated lattice positions and potentials with respect to the defined absorber atom. Make sure to change the ipot 0 element to the absorber species of interest.
Figure B.17 Screenshot of the resulting scattering paths from processing the Feff file.
3. Remember that the $\chi(k)$ spectra is a collective sum of all individual scattering paths between the absorber and its environment, and therefore the Fourier transform follows suit. Begin adding individual scattering paths to your fit within your region of interest. Artemis ranks scattering paths based on their theoretical influence on the total spectra. This may or may not be the case. In general, single scattering paths have highest influence of transform peak shapes. However, for anything above the first coordination shell, multiple scattering events need to be taken into account. Multiple scattering paths with a linear geometry or an obtuse triangle geometry play a more significant role in fitting than others, however keep in mind this is subjective, so it is best to try a variety of paths to determine significance. Figure B.18 shows the Fourier transform for J14-Ni with superimposed individual scattering paths.

![Figure B.18 Fourier transform of $\chi(k)$ for J14 Ni, with a Hanning window between 1.05 and 3.35 Å, containing the individual scattering paths that are using during the fit.](image-url)
4. A typical fit uses four parameters per scattering path. These parameters are $S_0^2$, $\Delta E_0$, $\Delta R$ and $\sigma^2$, as described above in B.1. $S_0^2$, $\Delta E_0$ are both properties of absorber species and once set, remain the same for all scattering paths. $\Delta R$ is the adjustment to the half path length, and for a single scattering path it is simply the adjustment in interatomic distance. This value typically does not exceed 0.5 Å. Define a variable for the $\Delta R$ of a particular single scattering path to a given coordination shell. For multiple scattering paths, use the same variable as the corresponding single path and create an equation describing the scattering geometry. An example of this is as follows: the $\Delta R$ for a Ni-O.1-Ni path is denoted delr0, and Ni-Zn.1-Ni path is denoted as delr1. Thus, for the triangular scattering path Ni-O.1-Zn.1-Ni the corresponding $\Delta R$ is $(\text{delr0} + \text{delr1} + \sqrt{\text{delr0}^2 + \text{delr1}^2})/2$. $\sigma^2$ essentially describes the contribution of thermal and static disorder that lead to variations in interatomic distances. Here, because the atoms in J14 are so similar in terms of x-ray scattering, a single variable is defined for each coordination shell. Multiple paths take the average of each scattering component. The last important note is that for a single scattering path, N is a coordination number, but for multiple scattering paths it serves as degeneracy. So keep in mind that if there are 12 next nearest neighbor cations distributed among 2 Co, 2 Ni, 3 Zn, 3 Mg, and 2 Cu atoms, a corresponding multiple scattering path with $N=48$ with have 8 Co, 8 Ni, 12 Zn, 12 Mg, and 8 Cu components. The point here is to make sure the math always makes sense before you do the fit so you cannot be falsely led.

5. The final step is to try the fit! Figure B.19 shows a fit using the scattering paths depicted previously. Upon completion of the fit, a report will appear detailing results shown at the end of this section. If the numbers make sense, the r-factor is acceptable, and you can defend your finding logically, you’ve successfully fit a theoretical standard. If not, try again. Just like anything else, skill is acquired through experience.
Figure B.19 Complete fit to the second nearest neighbor for J-14 Ni.
Figure B.20 Snapshot of fit report. $\sigma^2$ values less than 0.009 are ideal, but up to 0.05 is acceptable if static or thermal distortions are expected. A small $E_0$ means the absorption edge was chosen well. Half scattering path lengths determined by fit are in column $R$. Any severe deviations from what is predicted indicated a fit gone awry.
Appendix C  Additional Work

The following three studies were done during the course of this work for additional information on the J14 composition. C.1 and C.2 serve as quick references to Kissinger analysis and thermal expansion measurements, which provide quantitative descriptive parameters. C.3 briefly mentions work attempted with neutron diffraction studies, ultimately resulting in non-deal data for analysis, but should be highly considered as a measurement technique for future work.

C.1 Kissinger Analysis

To supplement and verify the result that shows the J14 phase transition is endothermic, we tried Kissinger analysis on J14. The Kissinger method is a very popular method for determining kinetic parameters via thermal analysis [154]– the basic premise is the assumption that under a constant heating rate the reaction rate of a chemical process is maximum where the DSC curve exhibits a peak. Further, if a series of measurements are done at different heating rates, a Kissinger plot can be plotted providing information on activation energy and pre-exponential factor. Figure C.1 shows a series of DSC curves demonstrating systematic peak shifts to higher temperatures as heating rate is increased. Using the equation

\[
\ln \left( \frac{\beta}{T_P^2} \right) = \ln \left( \frac{AR}{E_A} \right) - \frac{E_A}{RT_P} \quad (C.1)
\]

where \( T_P \) is the temperature of a peak maximum, \( \beta \) is the heating rate, \( A \) is the pre-exponential factor, \( R \) is the gas constant (8.314J/mol·K), and \( E_A \) is the activation energy, we can make a Kissinger plot, \( \ln(\beta/T^2) \) versus \( 1/T_P \), shown in Figure C.2. From this quick experiment, we gained two very important pieces of qualitative information.

1.) Our endothermic transformation is reproducible with a consistent heat of reaction.
2.) We can utilize the Kissinger method for future, more in depth work for ESOs and ergo treat their transformation like any other typical thermodynamic quantity.

*Figure C.1 Series of DSC plots showing the systematic shift in the endothermic reaction peak to higher temperatures as heating rate is increased.*
Figure C.2 Kissinger Plot of J14. The calculated activation energy for the reaction from multiphase to single phase is calculated to be 767 kJ/mol.
C.2 Linear Thermal Expansion of J14

One of the first studies done was determining the linear coefficient of thermal expansion of bulk J14. Using the non-ambient PANalytical XRD at the Analytical Instrumentation Facility (AIF), in-situ diffraction measurements were taken for a 2θ range of 35-45 ° at 100 °C increments. The ramp rate was 10 °C/min and an isothermal equilibration time of 10 minutes was held before each scan. The temperature spanned from 25 °-600 °C. The coefficient of linear thermal expansion was found to be $1.4 \times 10^{-5}/\degree C$. This value is on the same order to that of MgO [155] and NiO [156] both components in J14.

\[ \Delta L/L_0 = \alpha_L \Delta T \]
\[ \alpha_L = 1.4171 \times 10^{-5}/\degree C \]

Figure C.3 Plot of bulk J14 lattice parameter as a function of temperature. The inset shows the shift in (111) J14 peaks used to calculate lattice parameter. The coefficient of linear thermal expansion was found to be $1.4 \times 10^{-5}/\degree C$. 

206
C.3 Neutron Pair Distribution Function Study

Neutron PDF measurements were attempted at the Spallation Neutron Source beamline 1-B, NOMaD (Nanoscale Ordered Materials Diffractometer), under user proposal 13670.1. The purpose of this study was to complement the work done using EXAFS by looking at pair-pair correlations between J14 samples of varying Zn content. J14 bulk powders were measured against J14 (-10%) Zn and J14(+10%) Zn. Figure C.4 shows an example of the PDF from collected data between 1-10Å. Qualitatively, a trend that suggests lattice contraction and expansion with the removal or addition of Zn is apparent. Additionally, changes in peak shapes suggest deviations in correlation lengths.
Quantitative fitting using PDFgui [157] proved difficult due to the continually occurring over-fit/under-fit/over-fit pattern during the refinement process, shown in Figure C.5. After discussion with beamline scientists, this is found to be a common issue for samples that have a non-uniform grain packing distribution. Basically, this means that the powder sample was not milled uniformly enough to pack densely in the 3mm measurement capillary. So while amplitude-based information, such as species correlations, was unmanageable, we were able to find the lattice parameter of bulk J14 to be $4.2379 \pm 0.0002\text{Å}$. This once again agrees extremely well with the information from EXAFS and XRD.
Figure C.5 PDF of J14 measured at 100K demonstrating the undesirable fitting trend associated with poor sample packing density.

While this particular endeavor in neutron PDF did not work in our favor, it should still be considered in the future as a measurement technique. The scattering cross-section differences between neutrons and x-rays provide a complimentary contrast that will provide a better picture of the true structural nature of these systems.