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Versatile Synthesis of High Entropy Oxides (HEOs) by Aerosol Spray Pyrolysis

Ruby Aidun[1], James E. Park[1], Danny Drury[1], Bonnie McKenzie[1], Isabela L. Chou, Andrew De La Riva[2], Abhaya Datye[2], Elizabeth Paisley[1], Stanley S. Chou[1]*

1. Sandia National Laboratories, Albuquerque, NM
2. Department of Chemical & Biological Engineering, University of New Mexico Albuquerque, NM

* schou@sandia.gov

Background and Motivation

High Entropy oxides are multi-cation, single-phase oxides. HEOs have a high configurational entropy due to the multiple cations in the same lattice, thus stabilizing the structure.

We are developing facile, aerosol-based approach to rapidly prototype new HEO compositions and morphologies. HEOs have applications in catalysis, thermal barrier, structural ceramics and electroceramics. The tunable cation compositions and ratios allows for engineering of equilibrium and metastable defect states, when combined with nano and meso-scale morphological control, allows for tuning of hierarchical structures from angstroms to microns.

Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S$$

$$S_{con} = k_B ln(\Omega)$$

Ω = Number of Possible Configurations

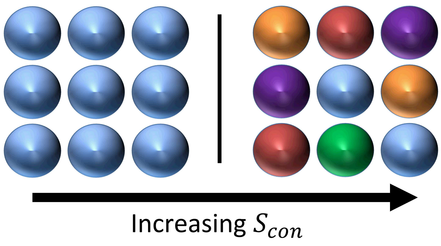
For a cubic system with N lattice points and arbitrary atomic ratios

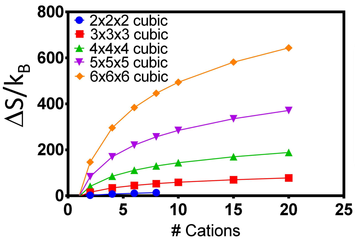
$$\frac{S_{con}}{k_B} = ln\left(\frac{x^N}{24}\right)$$

$$x \in (0, N)$$

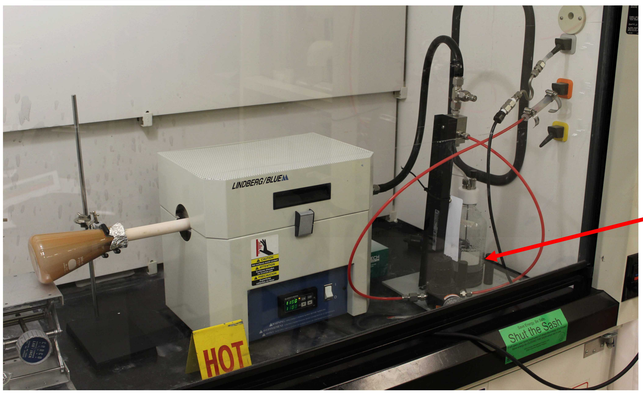
For an equimolar system with x type atoms, inside N lattice points

$$\frac{S_{con}}{k_B} = \frac{N!}{\left[\left(\frac{N}{x}\right)!\right]^x}$$

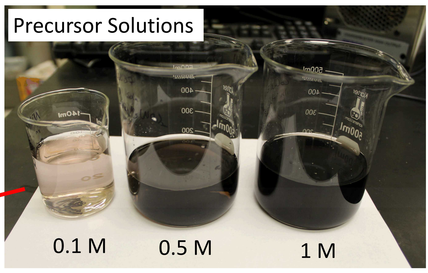




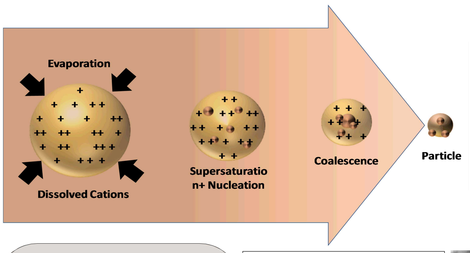
Higher number of cations & more lattice points => increasing configurational entropy.

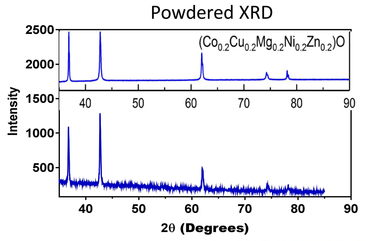


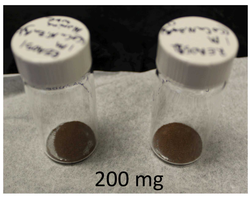
Solution Flow Rate: 3.43 mL/hr Gas Flow Rate: 35.5 mL/sec



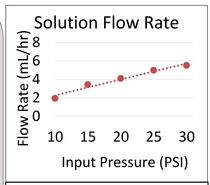
Mg^{12}	Co^{27}	Cu^{29}	Ni^{28}	Zn^{30}
Ionic Radii: 72 pm	Ionic Radii: L - 65 pm H –74 pm	Ionic Radii: 73 pm	Ionic Radii: 63 pm	Ionic Radii: 74 pm

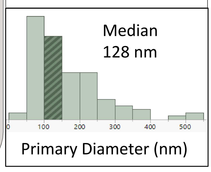


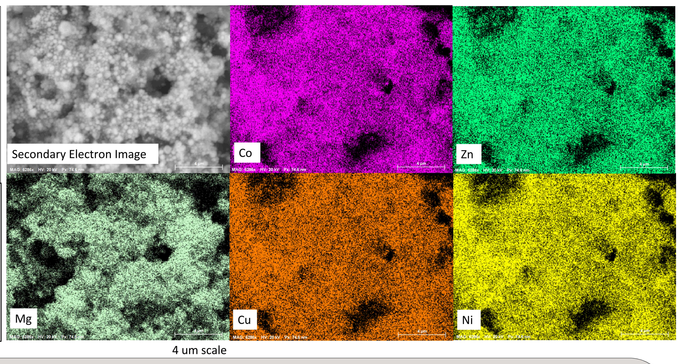




Particles form by super-saturation and nucleation as spray droplets evaporate. Fluid flow rate, controlled by gas pressure, dictates synthetic yield per unit time. Product exhibited requisite single-phase crystallinity and co-location of all precursor elements. Median diameter is 128 nm







Conclusions and Outlook

- Demonstrated scalable HEO synthesis using spray pyrolysis. This enables rapid turn-around from precursor to material, and prototyping of new compositions within 24 hours.
- We will incorporate soft-templates to enable hierarchical mesostructured with improved surface area.
- We will determine mechanical and thermal property of materials for structural ceramics and thermal barriers.
- We will explore deterministic precursor-structure-phase crystal engineering concepts available solely to High Entropy constructs.

References

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