Synthesizing morphology-controlled, high entropy perovskite nanomaterials for solid oxide fuel cells

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Background & Motivation

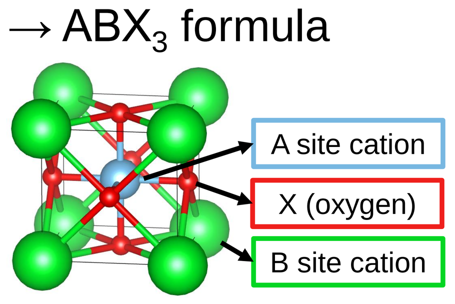
Motivation: Fuel cells to split water are a promising technology to shift to a clean energy economy. Current electrode materials in fuel cells use rare elements and need to last much longer to be scaled up for actual use.

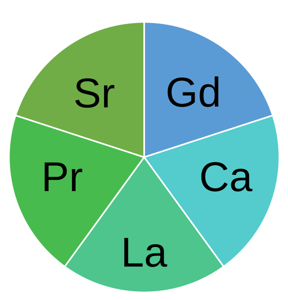
Project Goals

Electrocatalyst	• Including Fe and Co improves electrochemical performance
Perovskite crystal structure	• Promising structure for electrochemical applications, especially with earth-abundant elements
2D morphology	• Increases the number of available active sites
High entropy	• Stabilizes the inclusion of multiple species and causes a synergistic effect

Overview

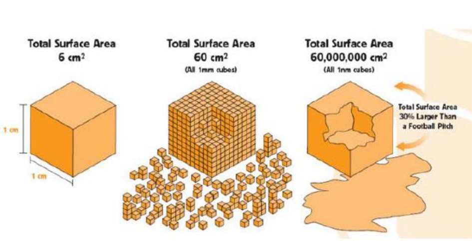
Perovskite structure
→ ABX_3 formula





A' site elements

2D nanomaterials
→ Thickness < 50 nm



High entropy
→ 5 different atoms on one site

Configurational entropy (S_c)

$$\Delta S_c = -R \sum c_i \ln c_i$$

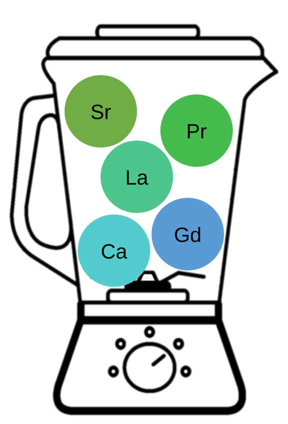
Universal gas constant; Mole fraction of element *i*

Gibbs Free Energy

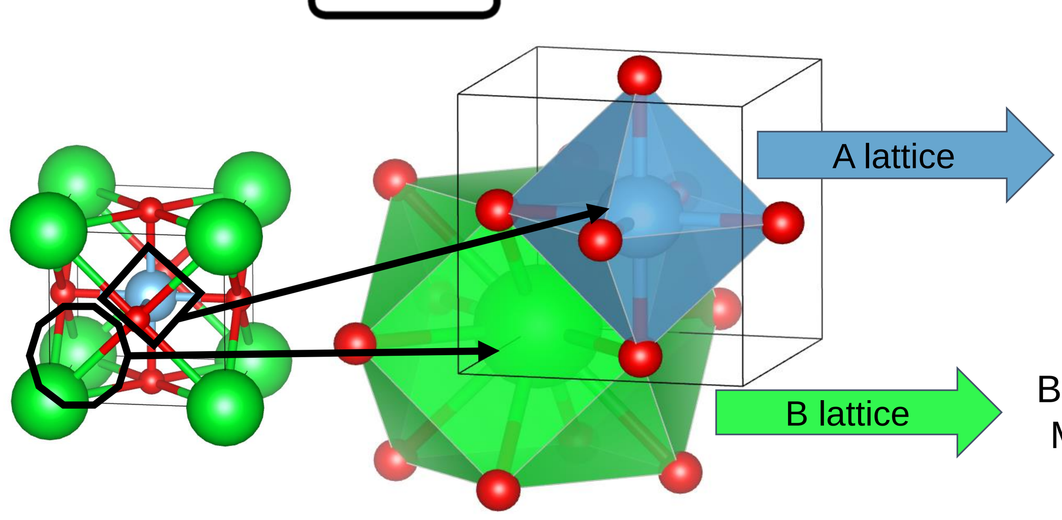
$$\Delta G = \Delta H - T\Delta S$$

Enthalpic term; Entropic term

High entropy requires random elemental distribution



This homogenous mixing produces a final material with properties distinct from the component elements, called the **synergistic effect**

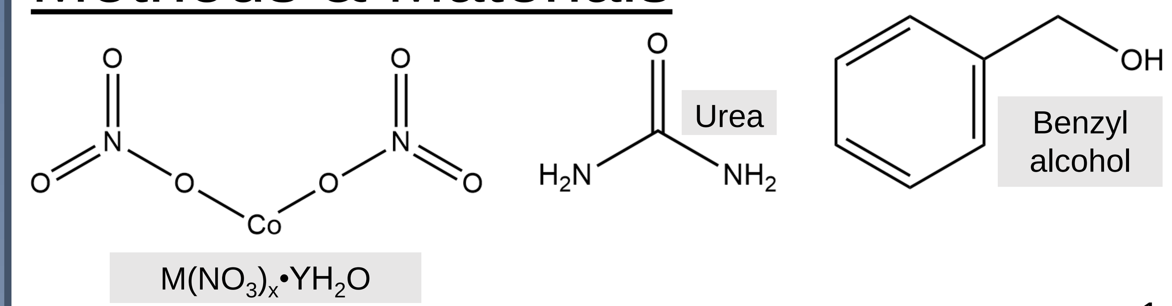


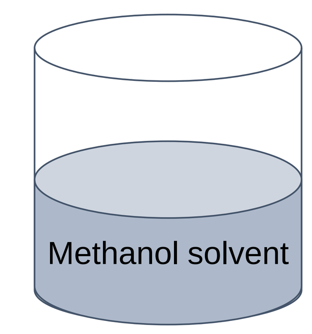
A site: La, Sr, Ba, Pr, Gd, Ca

B site: Cr, Ti, Mn, Co, Fe

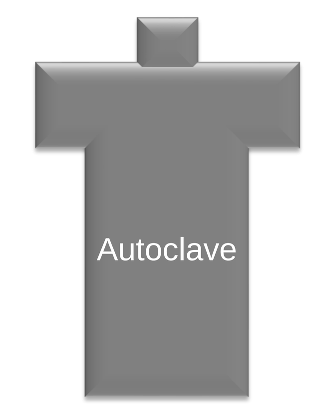
Hypothesis: Employing an autoclave method with a supercritical drying step will create nanomorphology and then a subsequent heat treatment will create a single phase, therefore making it high entropy.

Methods & Materials

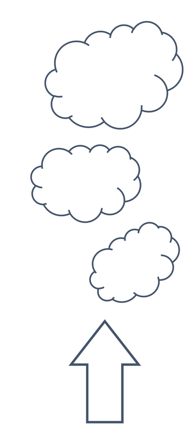




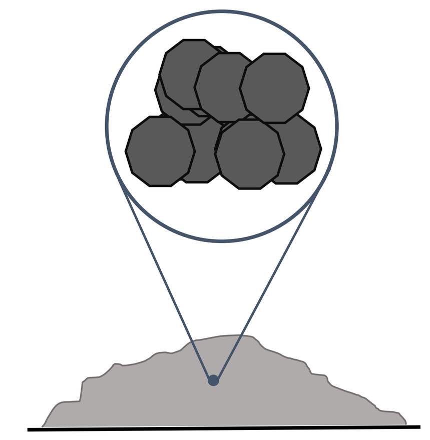
1. Stir and dissolve all chemicals in solvent



2. Autoclave is purged with inert gas and heated



3. Reactor pressure is released all at once to cause **supercritical drying**



4. Nanostructured powder product is acquired

5. Heat treatment forms a single phase

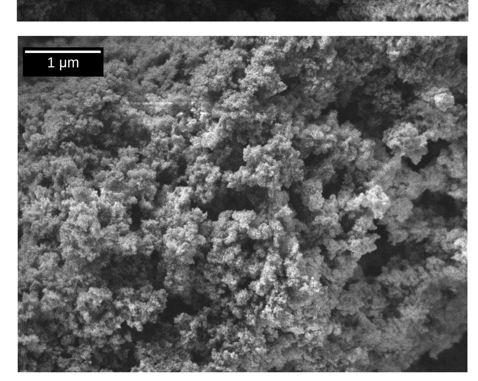
Challenge: How can a single phase be achieved without using high temperatures that destroy the nanomorphology?

Morphology

Benzyl alcohol is the **structure directing agent**, responsible for controlling the nanomorphology

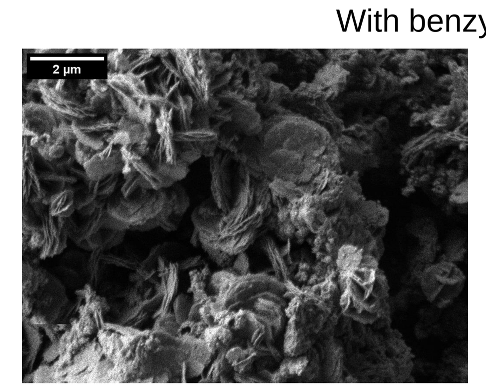
Scanning electron microscopy (SEM) shows the nanoparticle morphology with flakes and geometric shapes

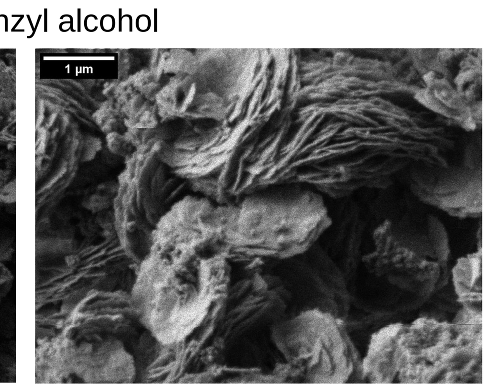
Without benzyl alcohol

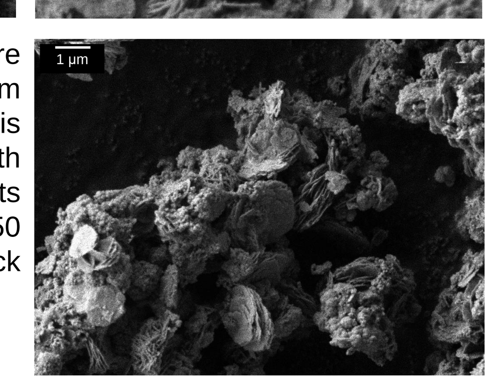


Non-uniform morphology visible with some geometric areas and small spheres

With benzyl alcohol







A much more uniform morphology is seen, with sheets averaging 50 nm thick

Acknowledgements

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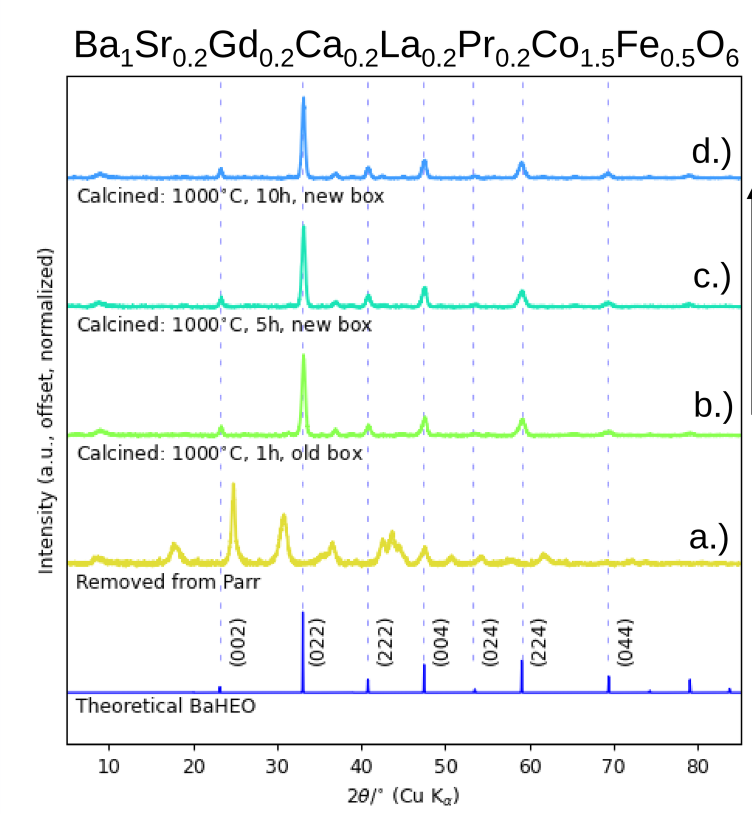
Richards Research Group

Let's connect on LinkedIn!

Sintering & Single Phase

Heating the removed product forms a single phase, but often causes particle size increase with time and temperature, called **sintering**

$Ba_1Sr_{0.2}Gd_{0.2}Ca_{0.2}La_{0.2}Pr_{0.2}Co_{1.5}Fe_{0.5}O_6$



X-ray diffraction shows the crystal structure and phases present in a material.

Increasing time

After heating, fewer peaks are seen, indicating a single phase forming

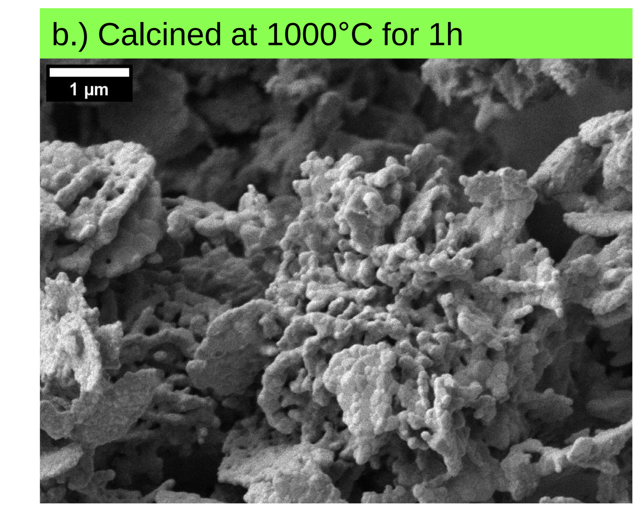
Product removed from reactor

Many peaks are seen, indicating multiple phases

a.) Removed from autoclave

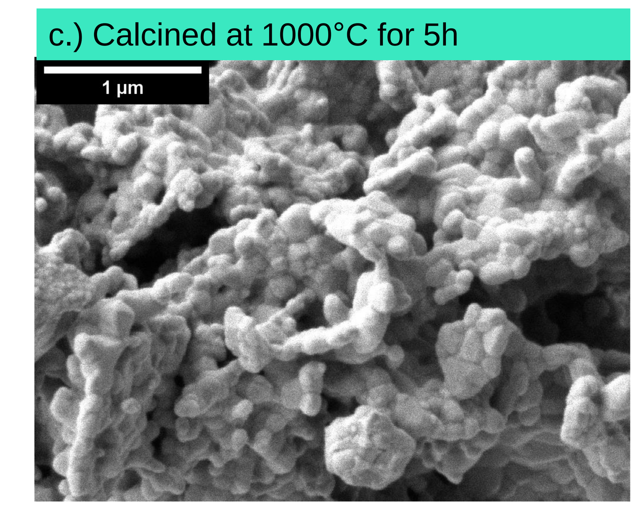
Some layered areas, large geometric and sintered particles

b.) Calcined at 1000°C for 1h



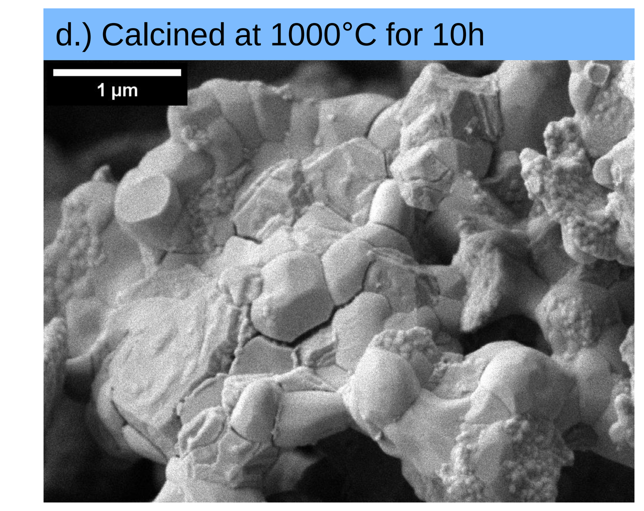
Thick plates made up of tiny geometric regions

c.) Calcined at 1000°C for 5h



Geometric regions grow, it now looks mostly connected

d.) Calcined at 1000°C for 10h



Mainly large and connected geometric particles remain, no sheets anywhere

Outlooks

Confirm composition of autoclave-prepared material
- Match composition of the nanomaterials to the bulk material $Ba_1Sr_{0.2}Gd_{0.2}Ca_{0.2}La_{0.2}Pr_{0.2}Co_{1.5}Fe_{0.5}O_6$

Apply templating methods to the powder product
- Templating could help form more consistent nanosheet morphology

Test electrocatalytic performance
- Compare nanomaterial performance to bulk materials

Consult computational results
- Apply the nanomaterial synthesis methods to other compositions that computationally perform better