Mixed-oxides for carbonaceous fuel conversion via chemical looping with oxygen uncoupling (CLOU)

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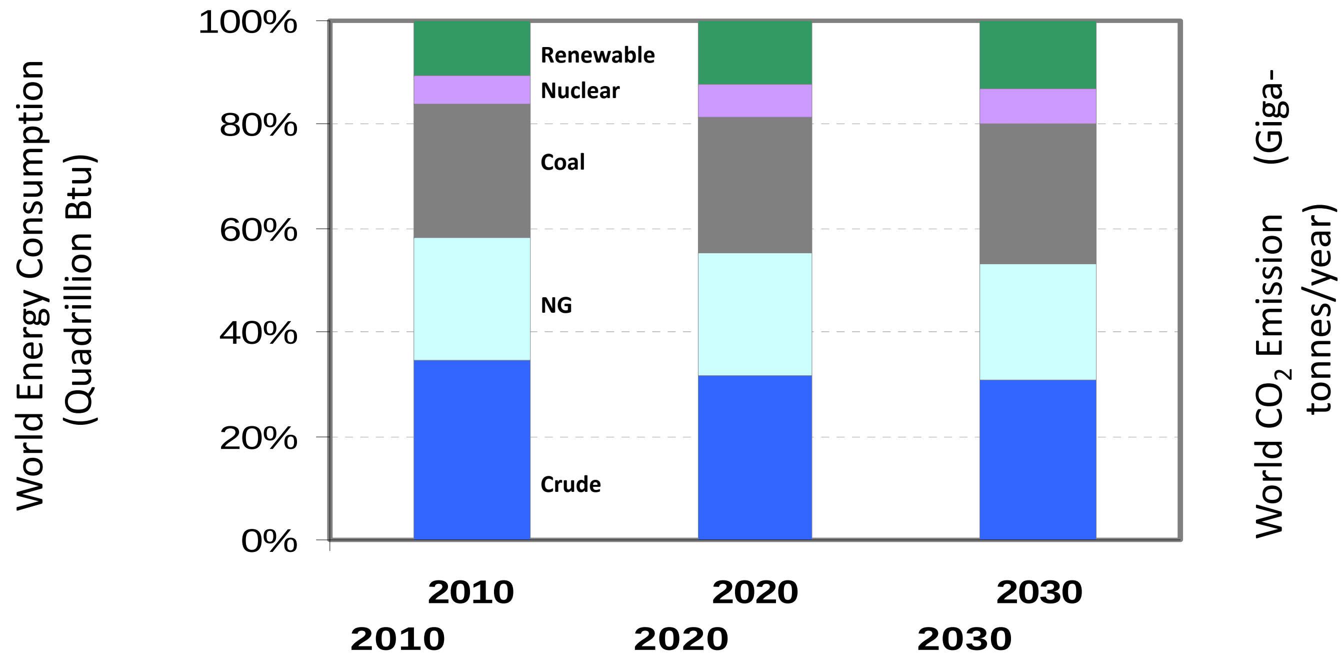
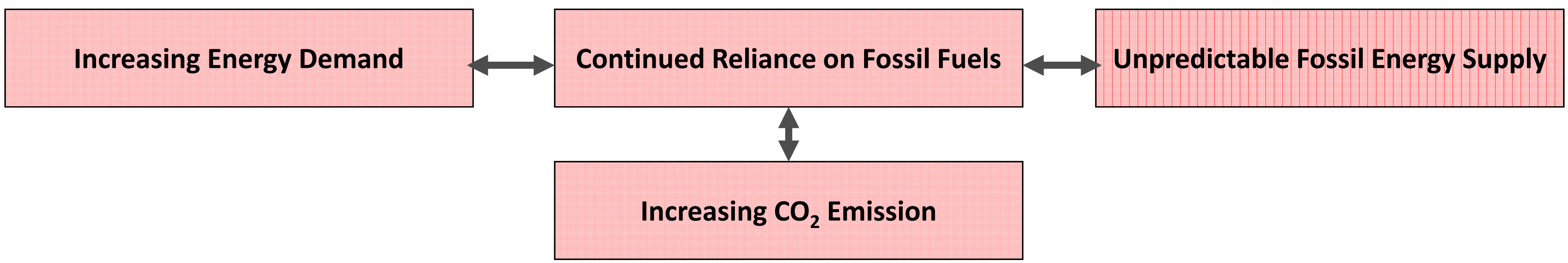
04/29/2015

Outline

- Background
- Perovskite Based Oxygen Carriers
  - Experimental investigation of A/B-site substitution effects
  - DFT investigation of substitution effects
- Perovskite Promoted Mixed Fe-Mn and Fe-Co Oxides
- Summary and Future Work

Background – World Energy Supply and Demand

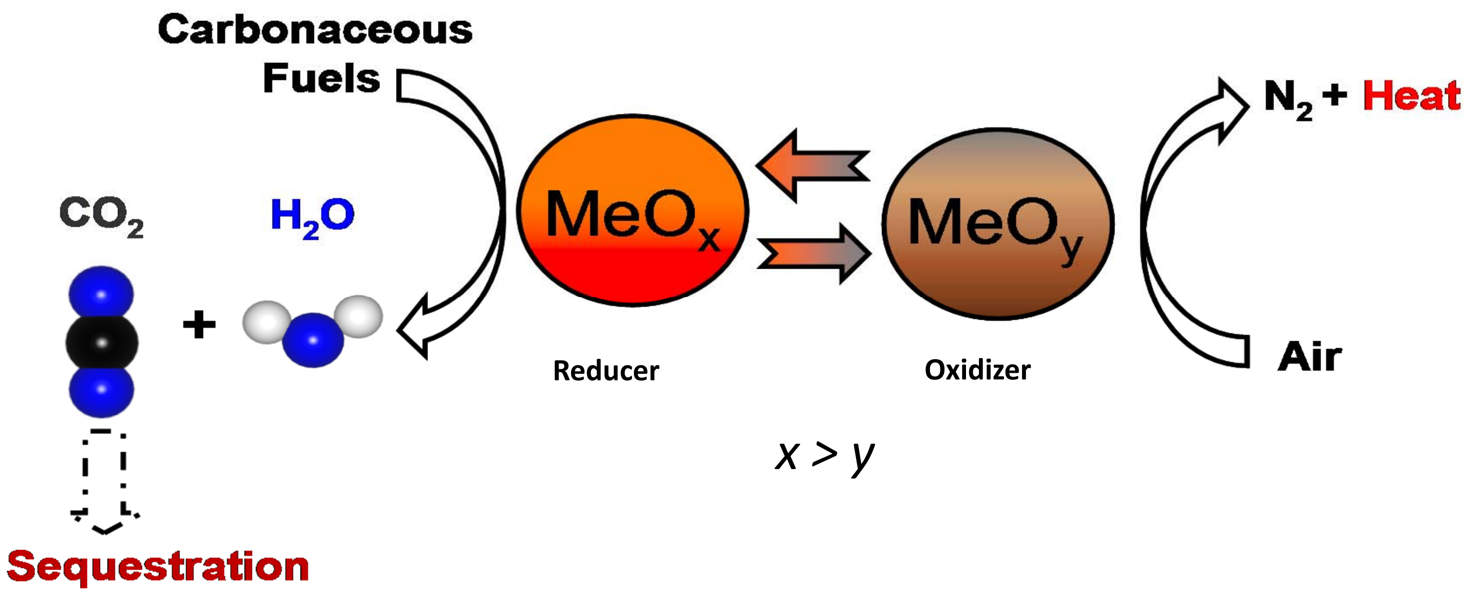




Carbon capture represents one of the key options for clean and sustainable usage of fossil energy

EIA, USDOE, International Energy Outlook

Chemical Looping Combustion (CLC)



CLC

- 2-Step Chemical Loop
- Fluidized Bed Reducer and Oxidizer
- Product: Heat, Power

Step 1: $MeO_x + Fuel \leftrightarrow MeO_y + H_2O + \mathbf{CO_2}$

Step 2: $MeO_y + Air \leftrightarrow MeO_x + N_2 +$ ***Heat***

Me can be Ni, Fe, Cu, Mn, Co, etc

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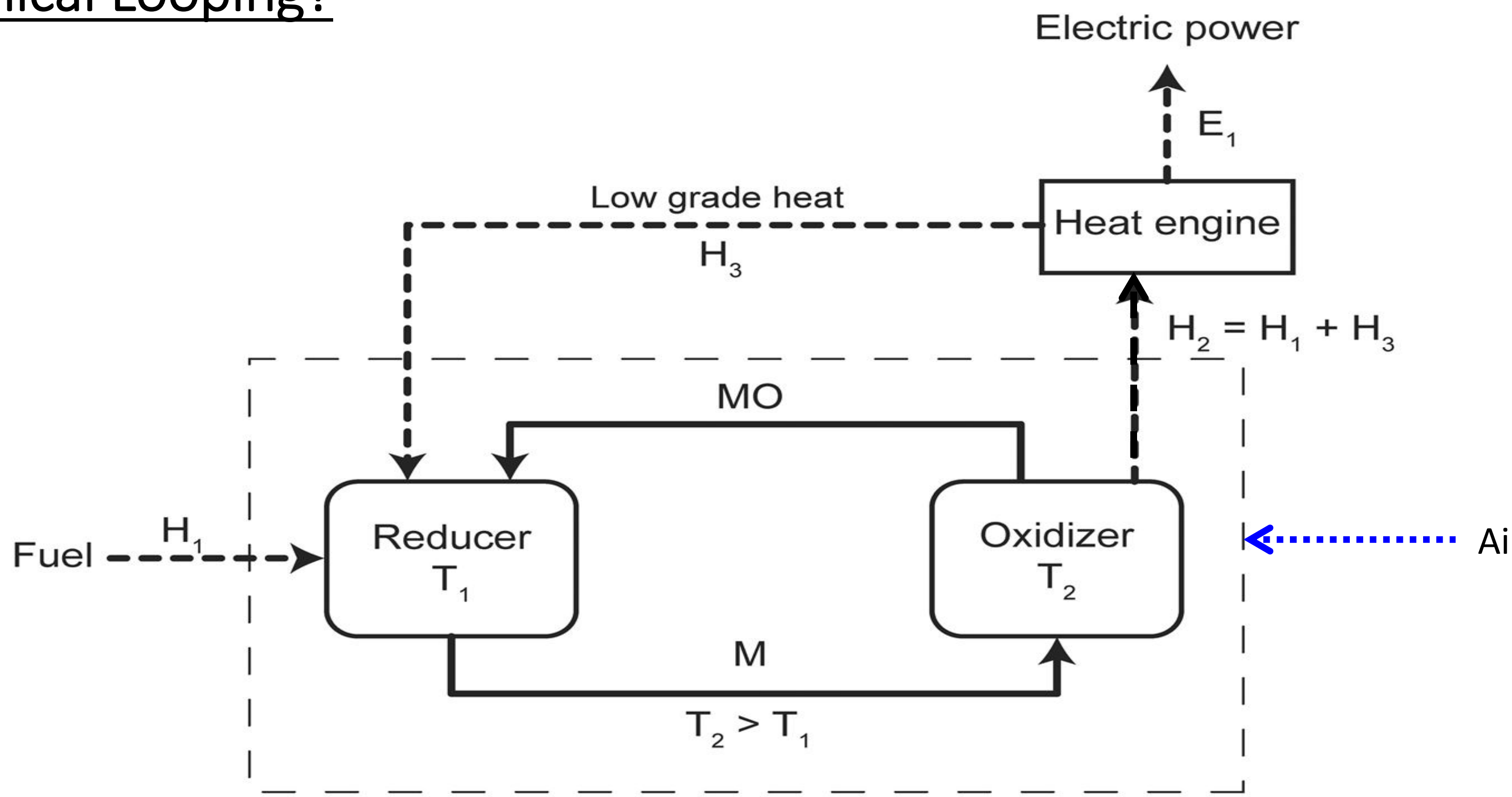
Why Chemical Looping?



Potential advantages of Chemical looping:

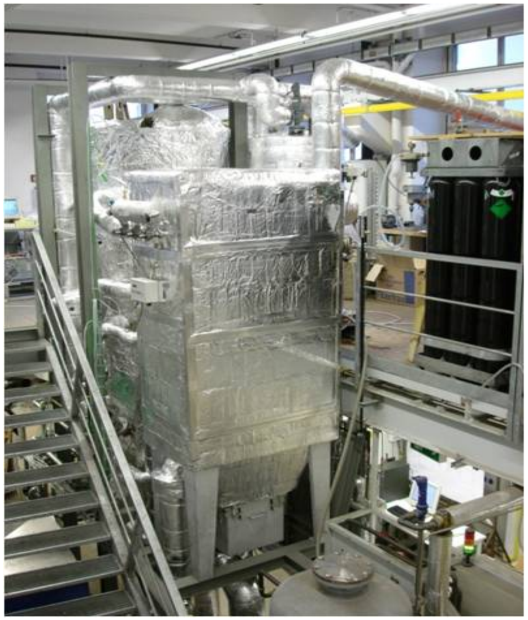
- **Tunable enthalpy extractible for heat engines through heat recuperation**
- **Fully integrated carbon dioxide separation cycle**
- **Delivery pressure of CO_2 can potentially be high**

Potentially higher 2nd law efficiency

Chemical Looping Processes – Status of Development

Ohio State University

Chalmers University of Technology



Vienna University of Technology

Korean Institute of Energy Research

kW and MW-scale demonstration plants have been constructed and operated

Photos curtsey of Chalmers University of Technology, Ohio State University, Vienna University of Technology, and Korea Institute of Energy Research,

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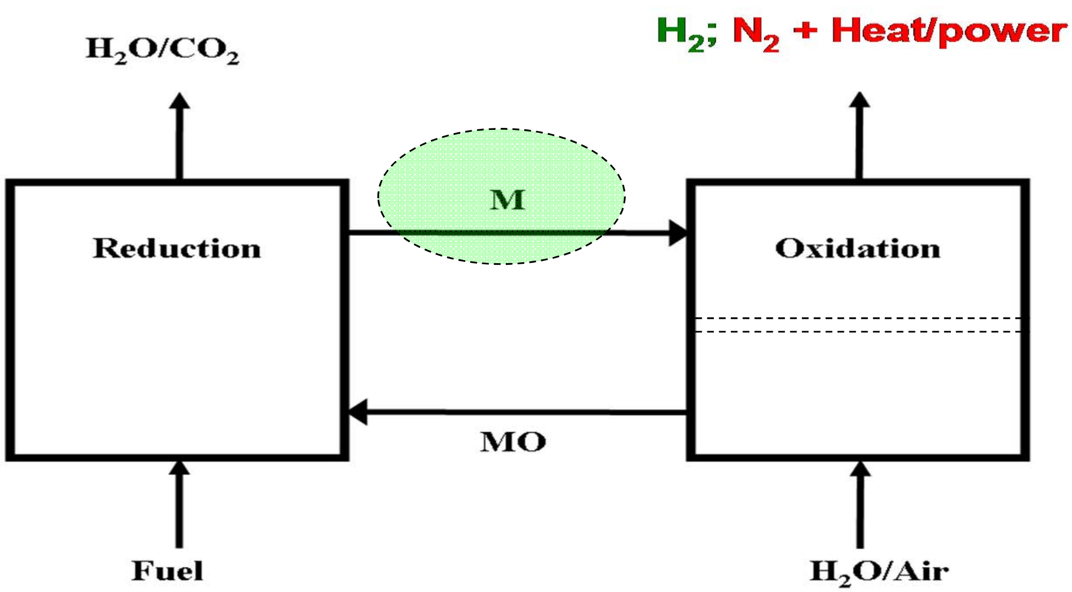
Chemical Looping Processes – Advantages and Challenges



Common Features

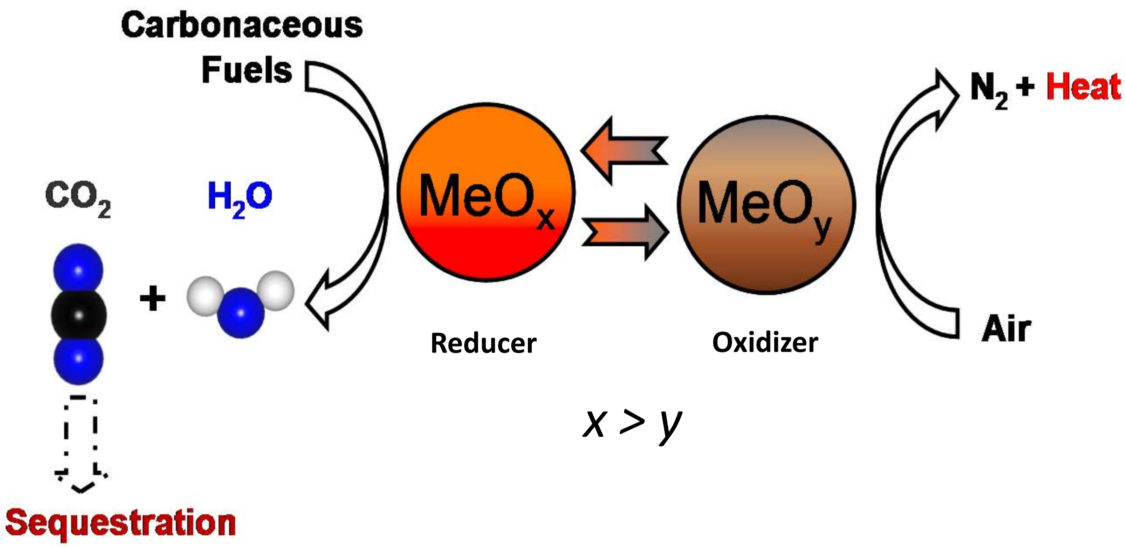
- Integrated Product Separation
- Metal Oxide Redox Reactions
- Potential Exergy Recuperation

Keys to Success:

1. ***Oxygen carrier particles*** **with good reactivity, recyclability, and strength;**
2. *Reactor design* that can effectively convert and circulate oxygen carrier particles

Fan L-S. Chemical looping systems for fossil energy conversions. John Wiley & Sons, 2010

Chemical Looping Combustion for Solid Fuels - Challenges



$6Fe_2O_3 + C \leftrightarrow 4Fe_3O_4 + \mathbf{CO_2}$ **Very slow!**

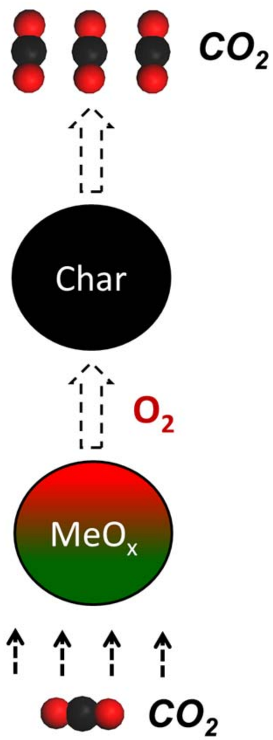
Solution: *In-situ gasification of solid fuel*

$C + H_2O/CO_2 \leftrightarrow CO + H_2$ **Still quite slow**

$3Fe_2O_3 + CO/H_2 \leftrightarrow 2Fe_3O_4 + CO_2/H_2O$

Low solid fuel conversion due to slow solid-solid reaction rate

Accelerated Solid Fuel Conversion – Chemical Looping with Oxygen Uncoupling (CLOU)



Underlying principle:

- Use of oxygen carriers that allow facile exchange of lattice oxygen with external environment under varying oxygen partial pressures
- Oxygen releases help combust the coal char and volatiles

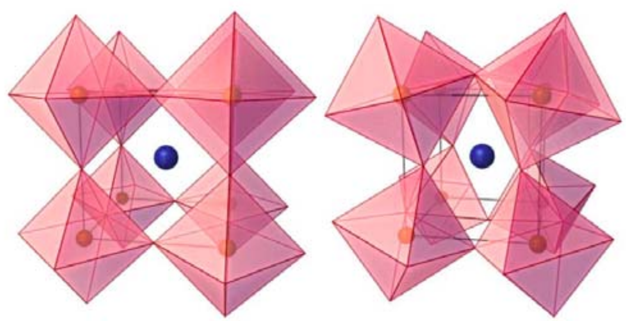
Challenges:

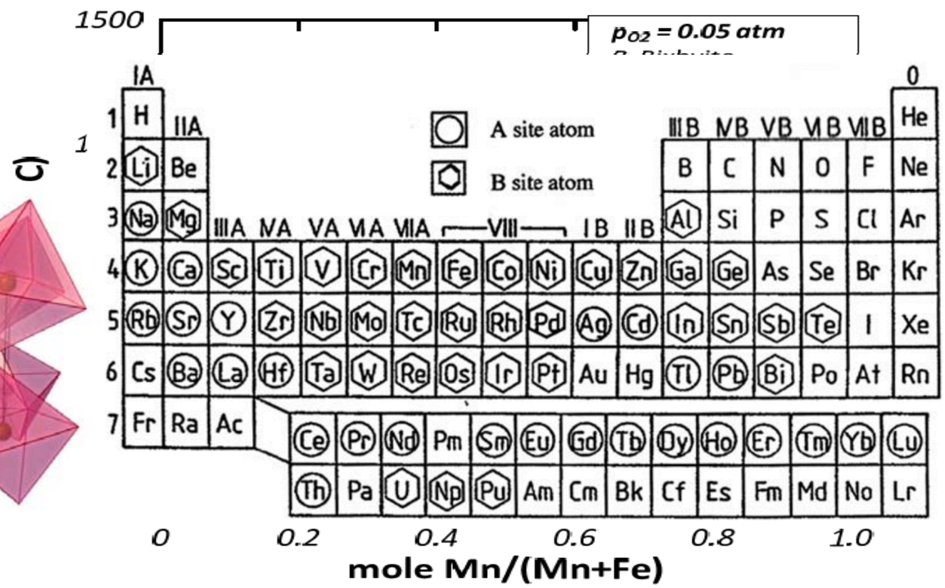
- Developing oxygen carriers with:
  - Spontaneous release of lattice oxygen into gas phase
  - Easy re-oxidation in air
  - Structural integrity and oxygen carrying capacity

Material Selection – Rapidly Expanding Material Design Space

Recent developments in oxygen carrier materials

- Iron
- Copper
- Manganese
- Nickel
- Cobalt
- Perovskite materials
- Mixed first row transition metal oxides





M. Rydén et al., 2nd International Conference on Chemical Looping, 2012
Structure and Properties of Perovskite Oxides, Tatsumi Ishihara

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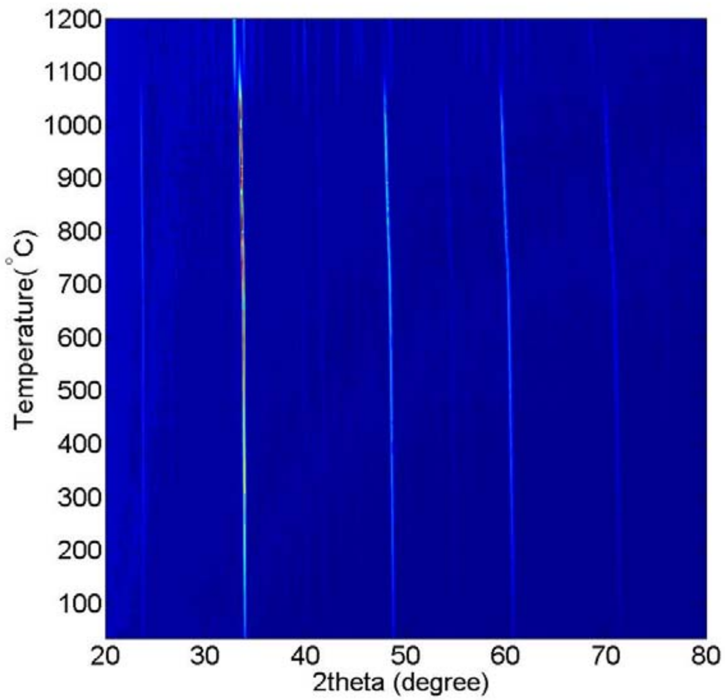
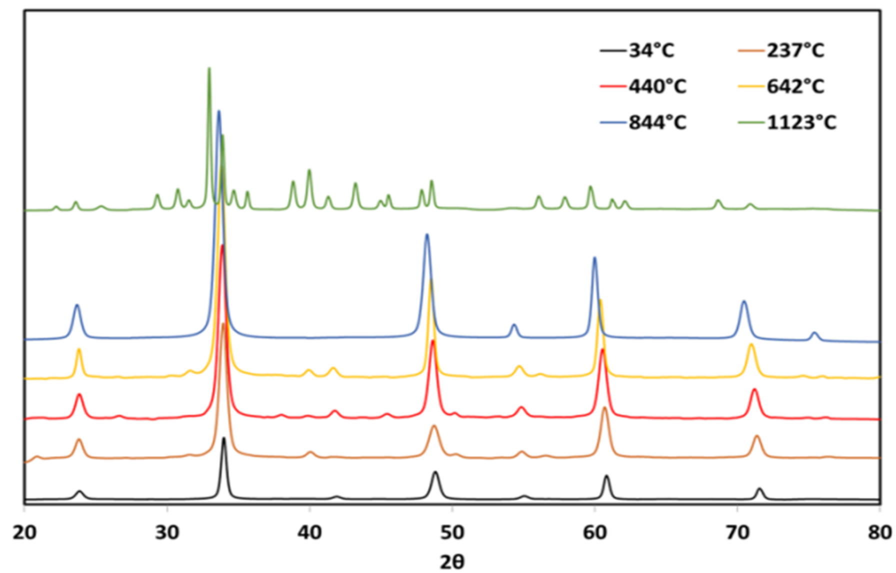
Stability of $CaMnO_3$: *In-Situ* XRD Studies

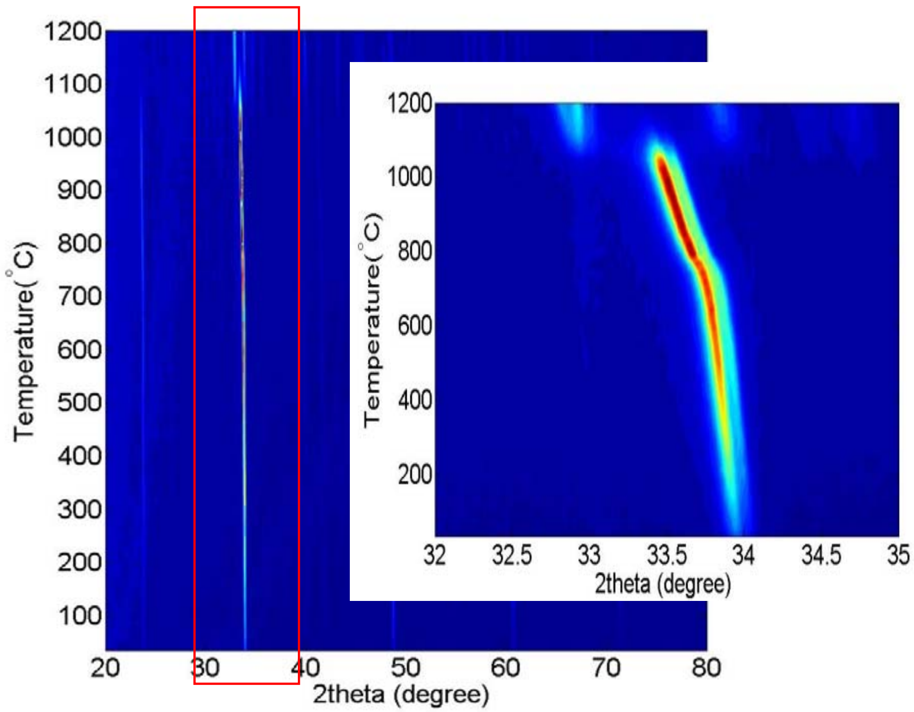


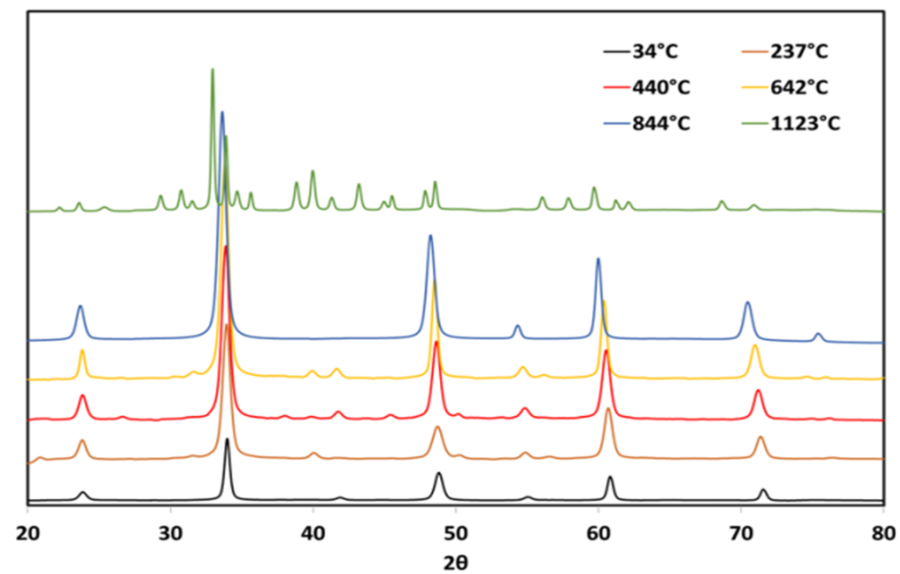


$CaMnO_3$ is chosen as the base material due to its well-known CLOU Properties

- Peaks begin to significantly shift between 800-850°C ; sign of oxygen uncoupling
- Up to 1100°C cubic $CaMnO_{3-\delta}$ remains stable

Stability of $CaMnO_3$: *In-Situ* XRD Studies



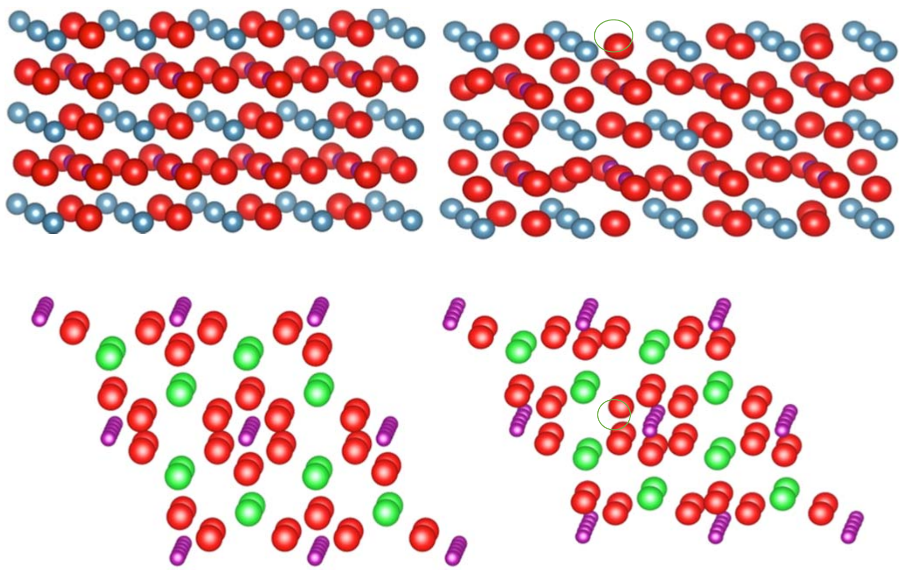


- After 1100°C spinel $CaMn_2O_4$ and Ruddlesdon-Popper Ca_2MnO_4 phases form
- *Irreversible phase transition also observed under isothermal cyclic conditions at lower temperatures*

Motivation for Dopant Addition

$CaMnO_3$

$BaMnO_3$



Primary Perovskite Material	$CaMnO_3$
A-site Dopants	**Ba and Sr**
B-site Dopants	**Fe, Co, Ni, V, Al**

DFT calculation of vacancy formation energy

	E_{O_V}, FM (eV)	E_{O_V}, AFM (eV)
$BaMnO_3$	2.79	3.18
$CaMnO_3$	2.59	2.63

Testing Conditions:

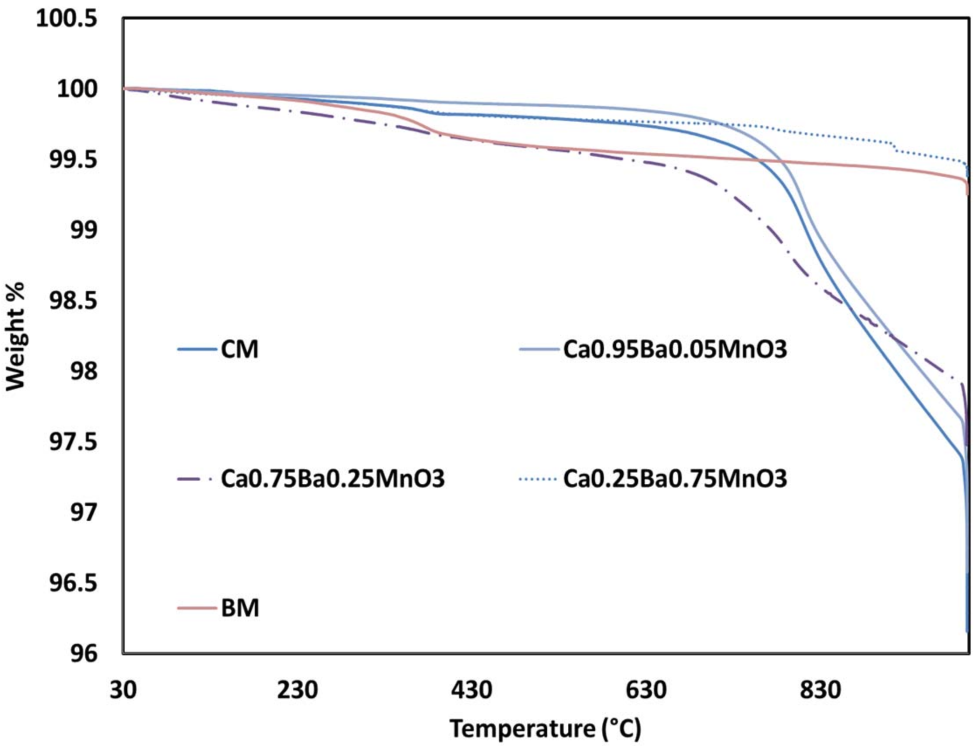
T: 650-1200°C

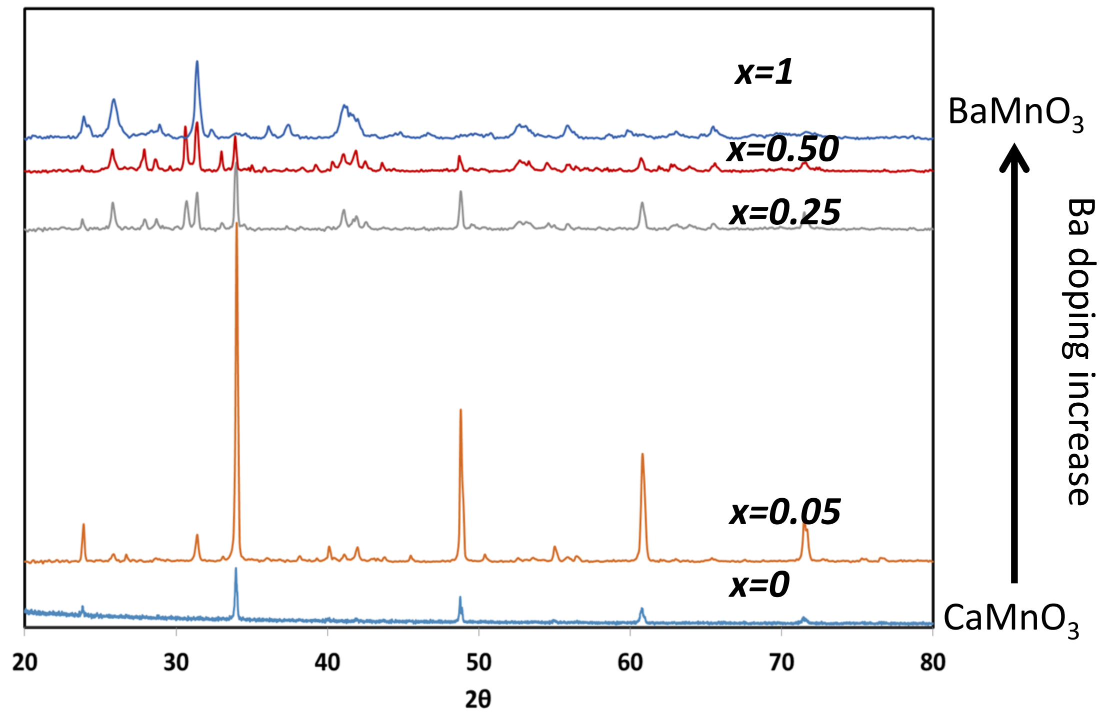
P_{O2}: <<0.01-0.10atm

Experiments:

1) (*In-situ*) XRD
2) Temperature programmed desorption (TPD)
3) Isothermal (chemical looping) cycling
4) Redox cycles with solid fuel

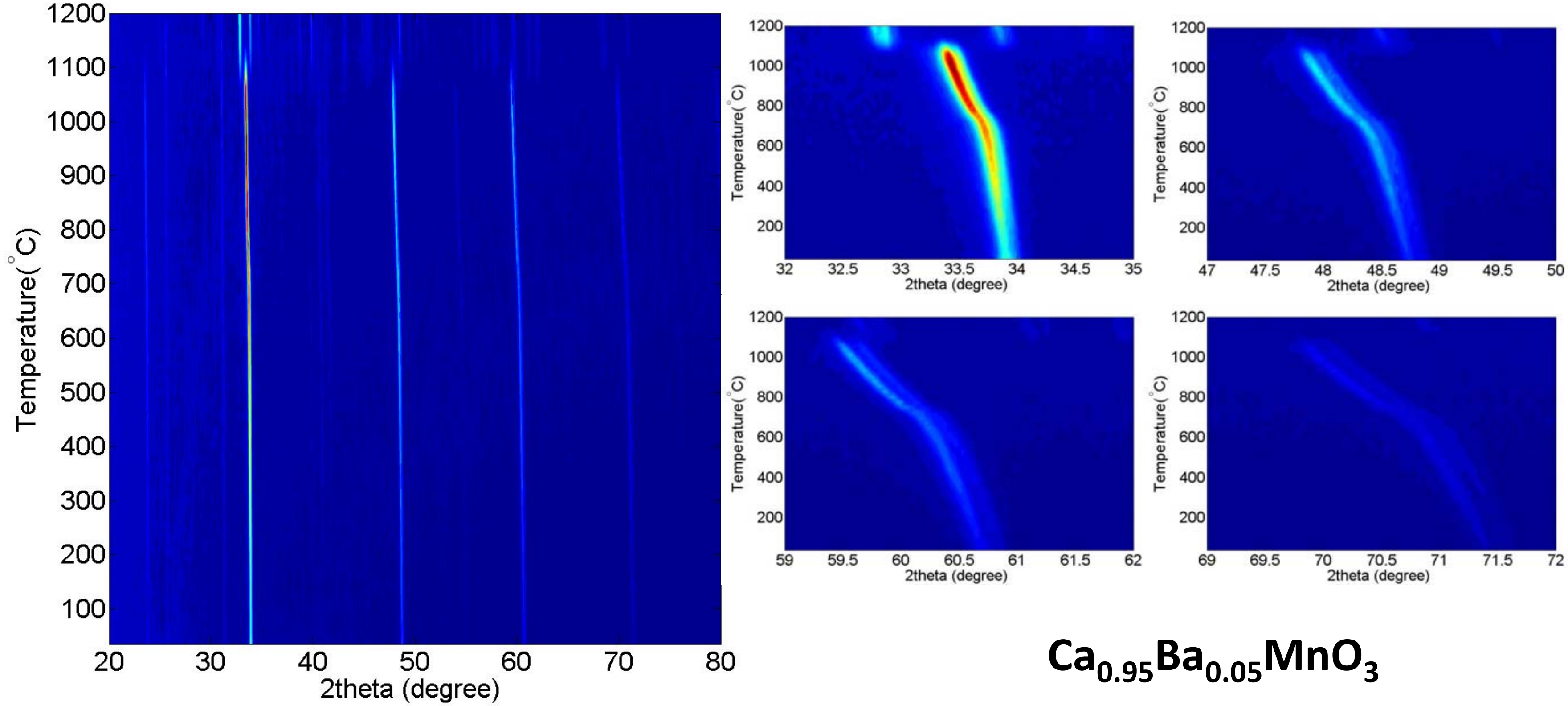
Effect of A-site Substitution for $CaMnO_3$- Barium





Ba dopant is largely immiscible with the $CaMnO_3$ structure, Ba doped samples also showed poor redox stability

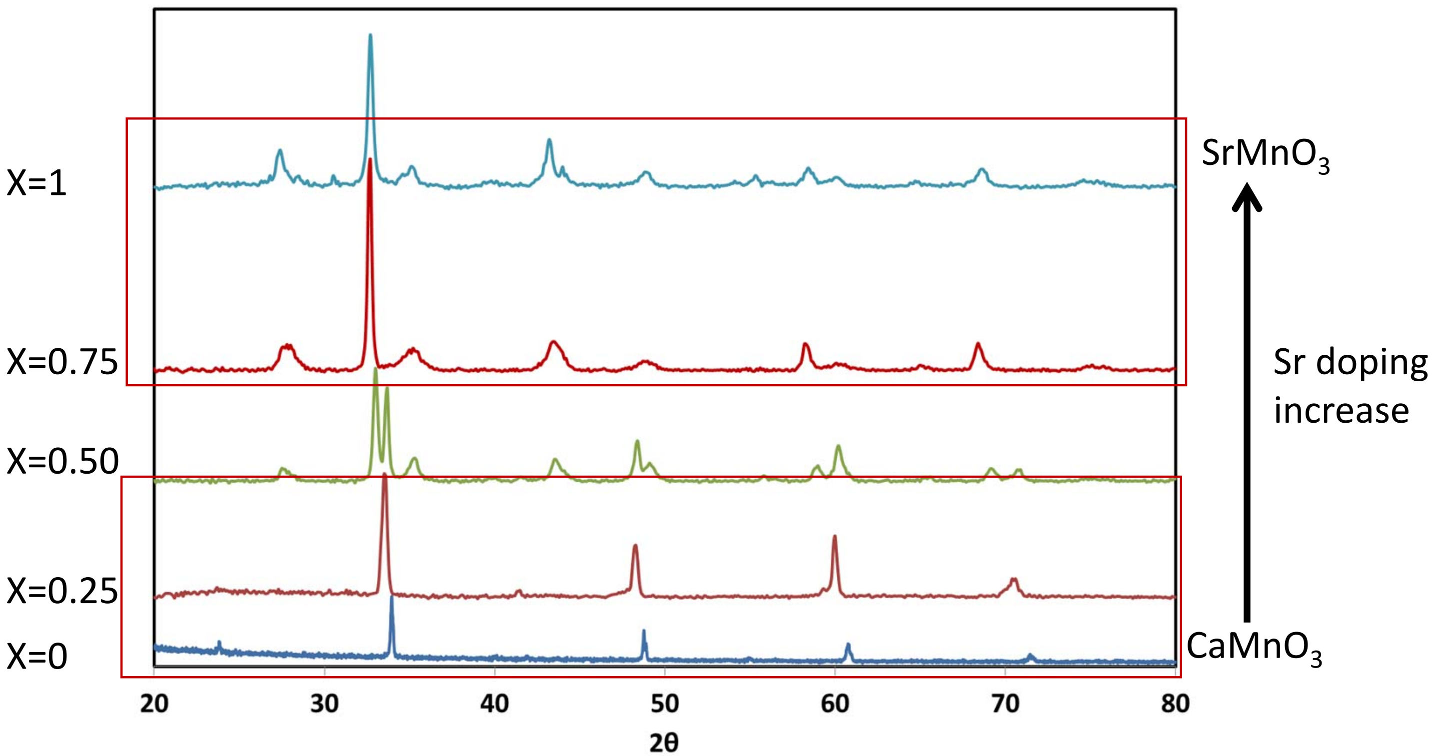
Effect of A-site Substitution for $CaMnO_3$- Barium



$Ca_{0.95}Ba_{0.05}MnO_3$

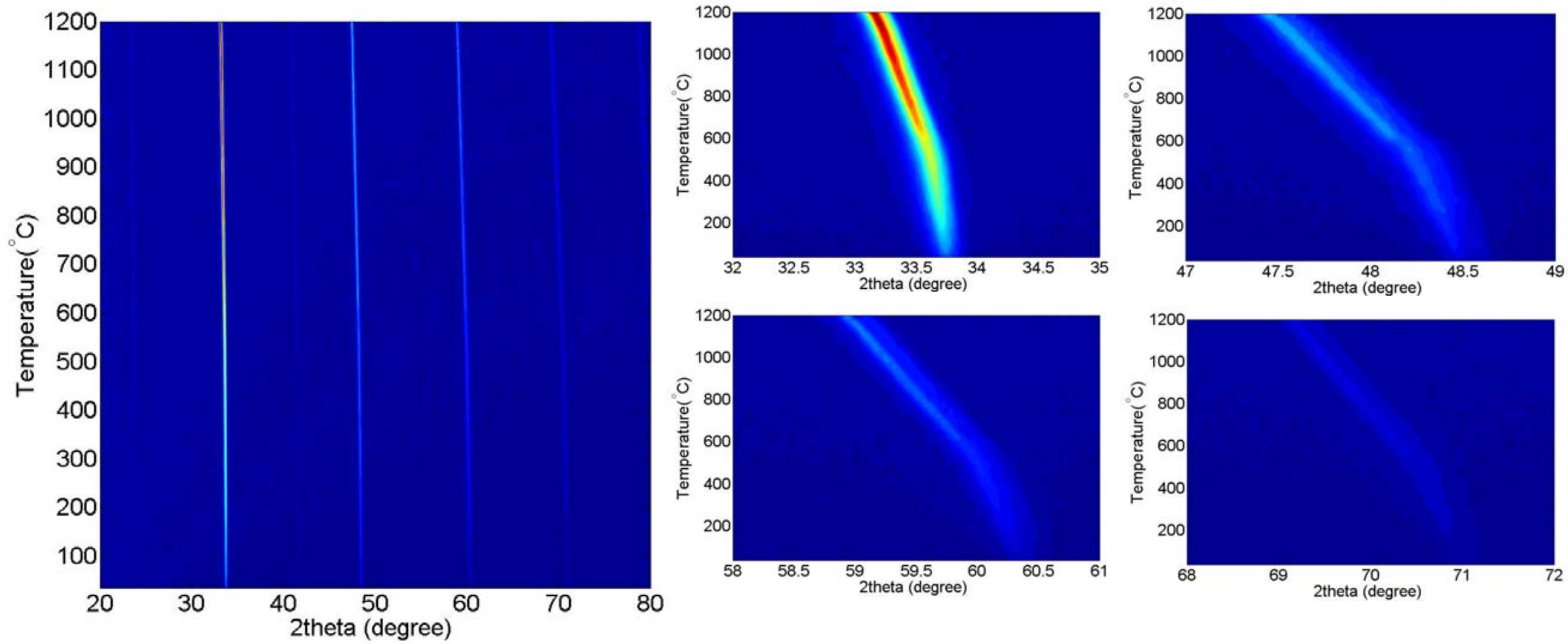
Ba substitution is ineffective to prevent irreversible phase change of $CaMnO_3$

Effect of A-site Substitution for $CaMnO_3$- Strontium



Sr forms well defined solid solution with $CaMnO_3$

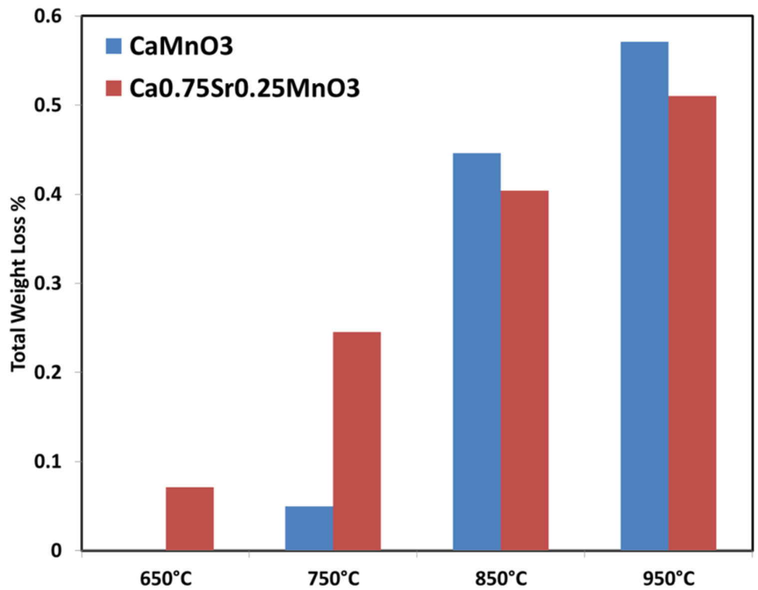
Effect of A-site Substitution for $CaMnO_3$- Strontium

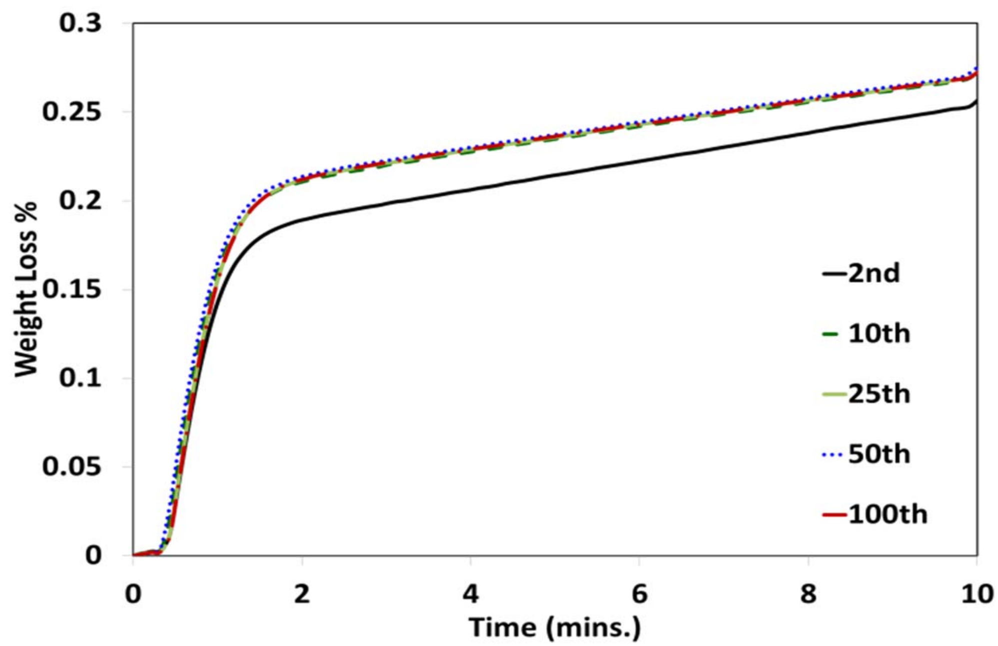


$Ca_{0.75}Sr_{0.25}MnO_3$

No irreversible phase transition observed up to 1200 °C

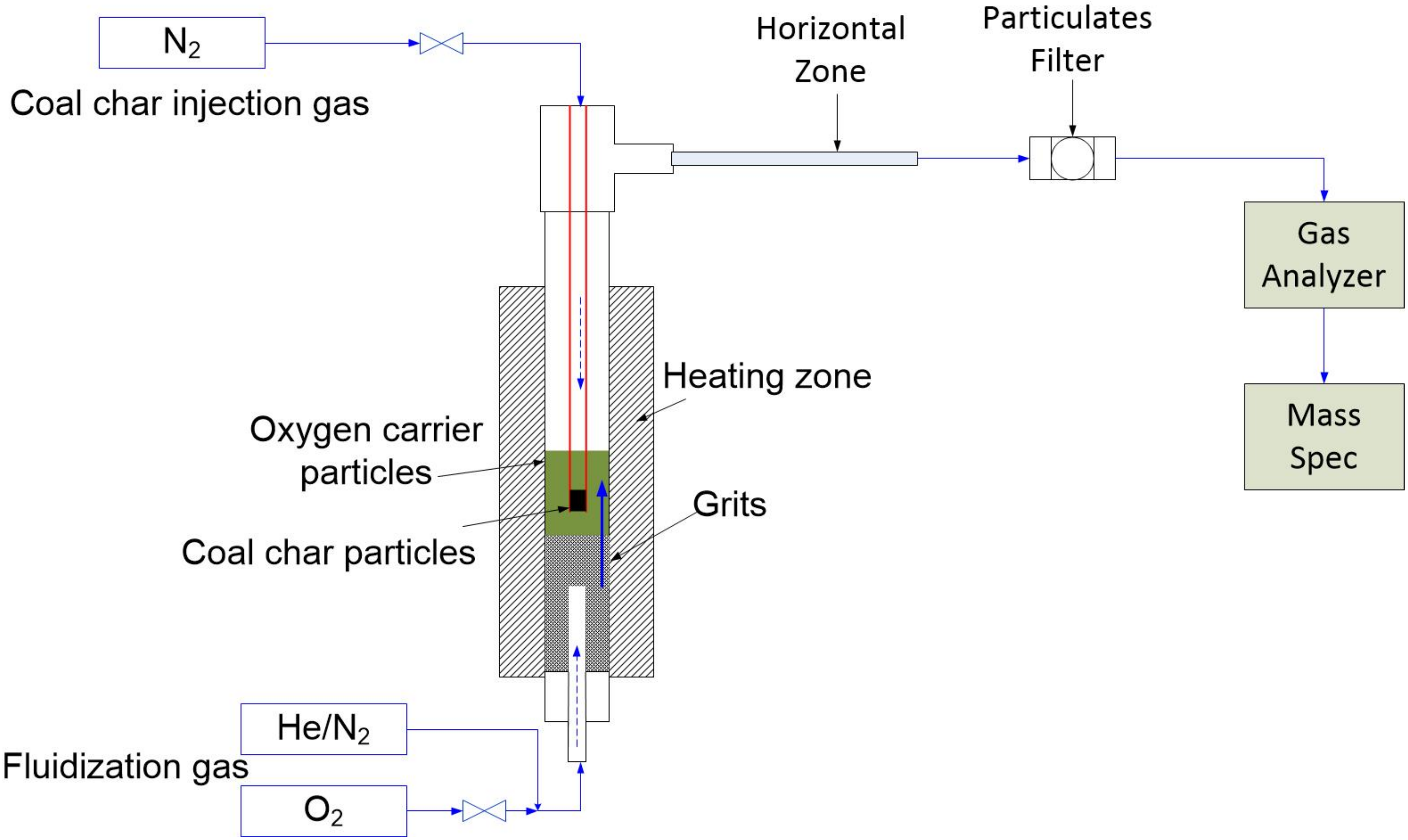
Isothermal CLOU Experiments



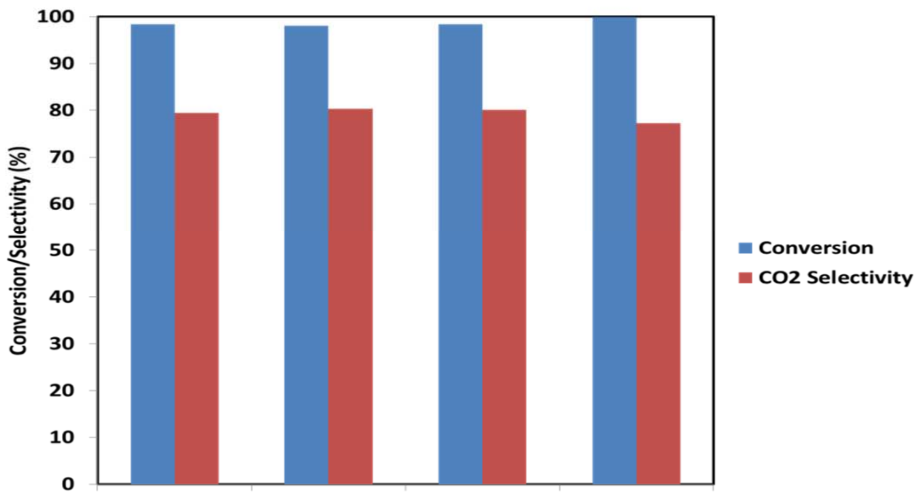


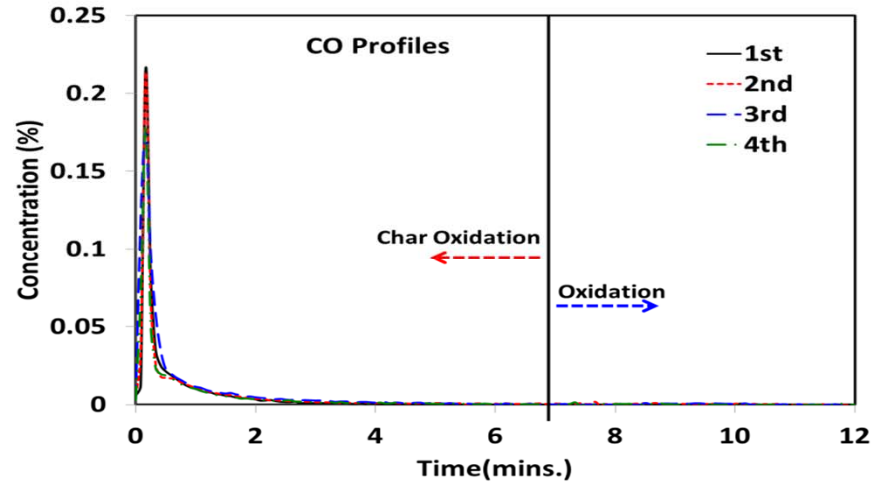
$Ca_{0.75}Sr_{0.25}MnO_3$ is redox active down to 650 ˚C and recyclable for 100 cycles, while $CaMnO_3$ is relatively inactive until above 800°C

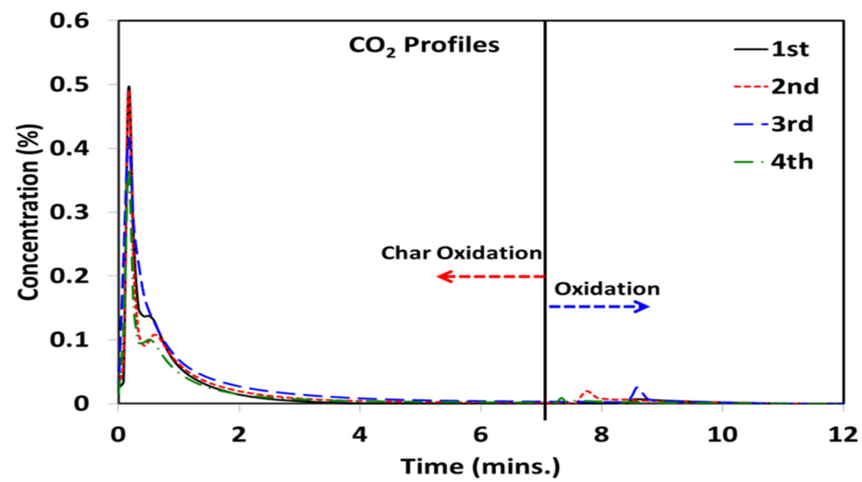
Fluidized Bed Setup



Fluidized Bed Experiments



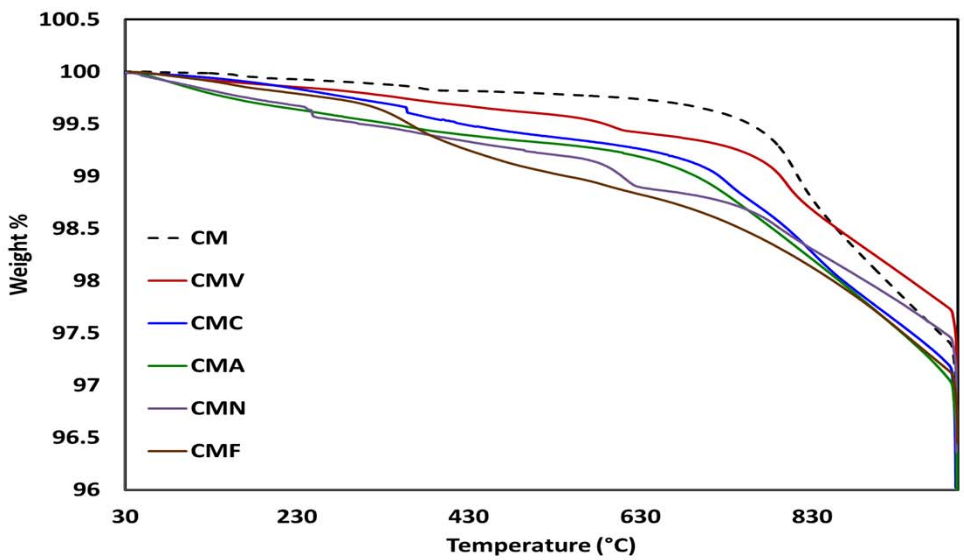


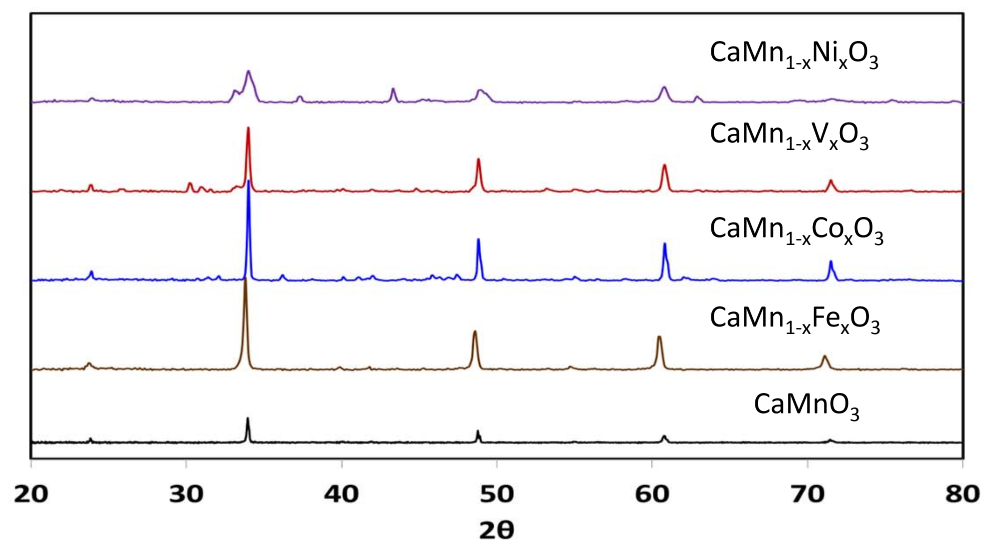


Char cycles after 20 hours operation in helium/10% O_2 redox mode (~60 cycles) and 10 other char cycles spread throughout the 20 hours of operation

Temperature: 850°C
Fluidization velocity: 6 times of U_{mf}
Coal Used: Sea coal (bituminous)
Attrition rate: <0.02%/hour

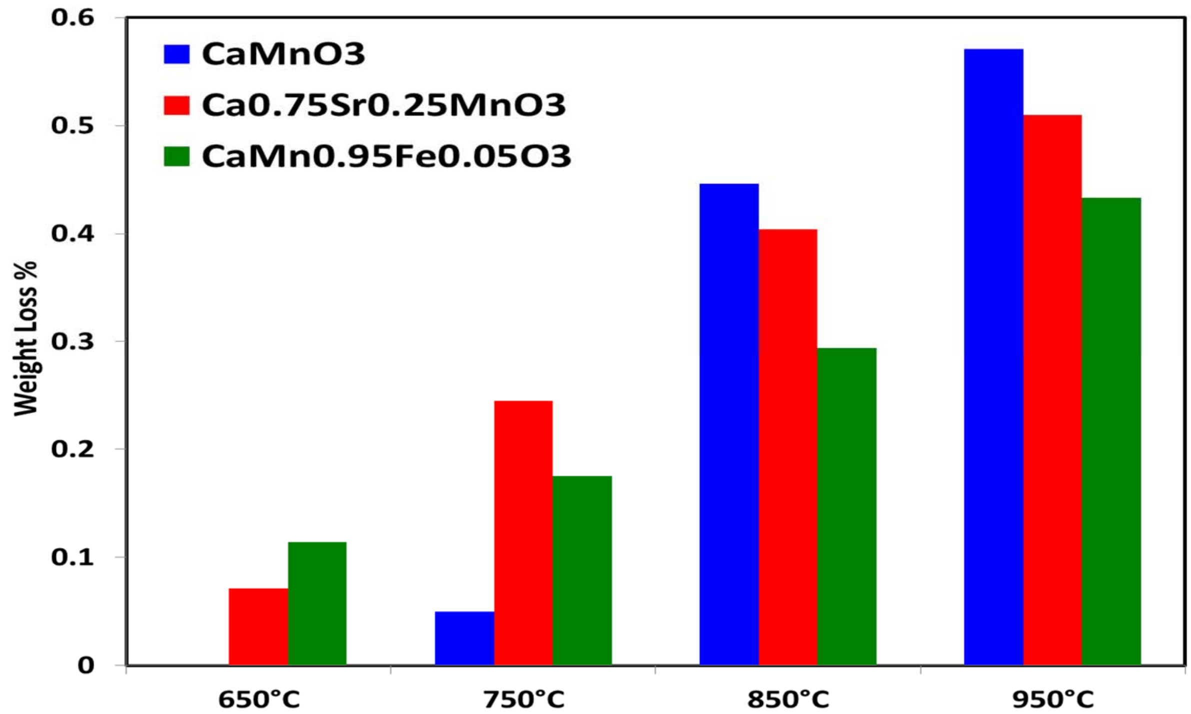
Effect of B-site Dopants





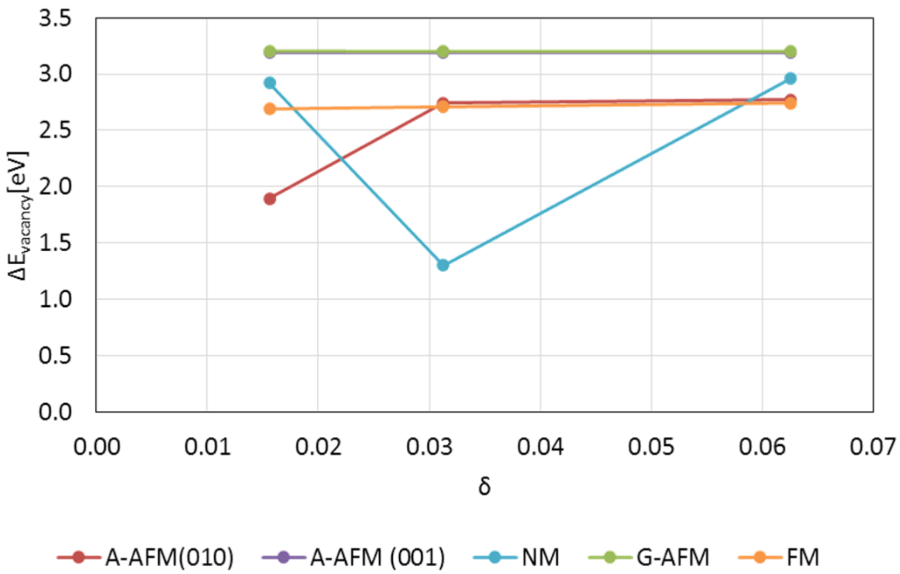
B-site substitution also leads to oxygen carriers with varying redox properties

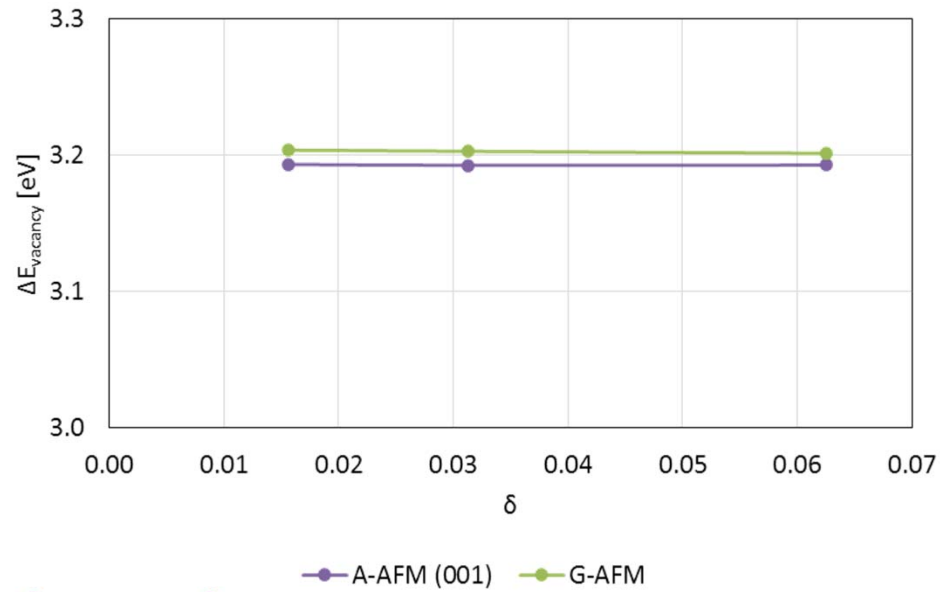
Isothermal Redox Experiments



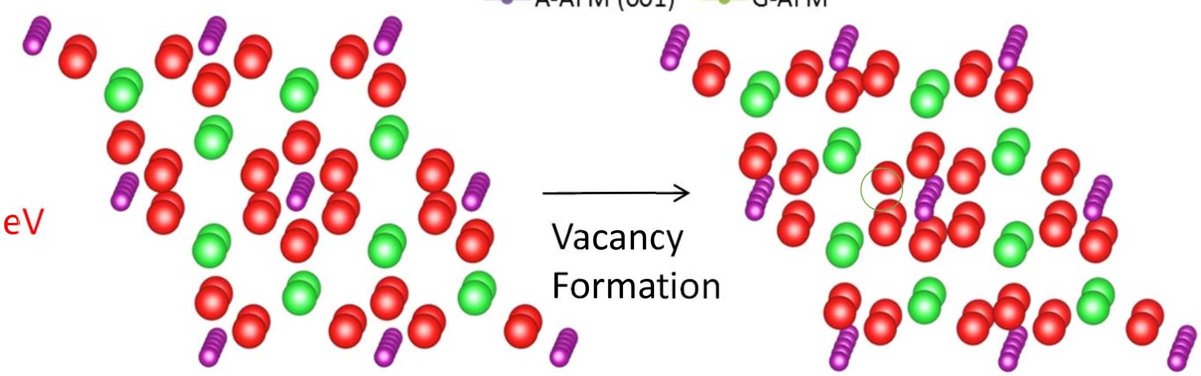
Iron doped $CaMnO_3$ exhibits excellent redox activity under low temperatures

DFT Investigation: $\Delta E_{vacancy}$ (Hexagonal $BaMnO_3$)

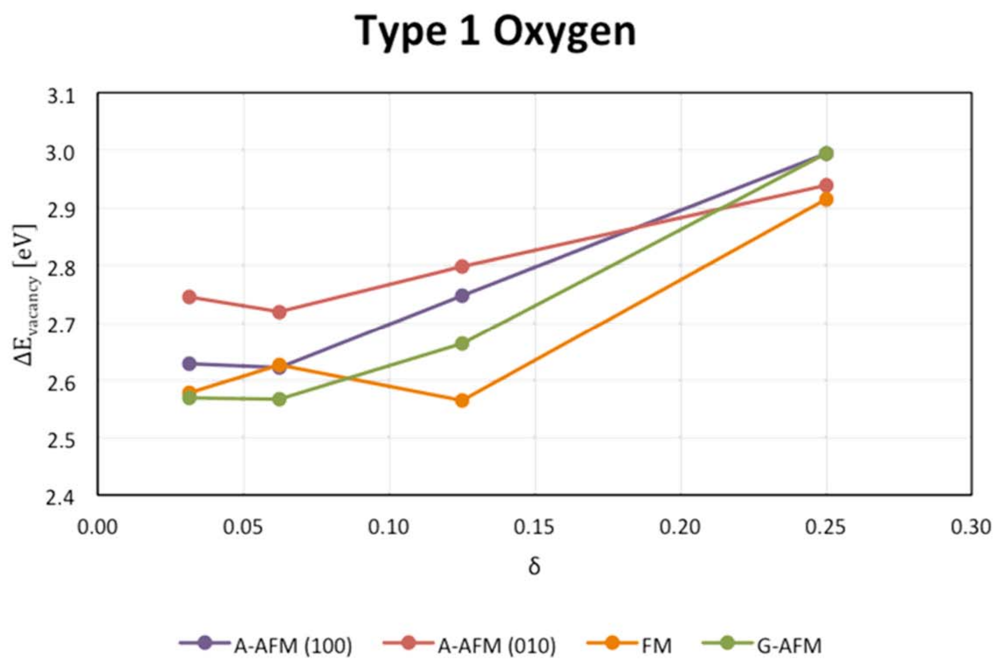


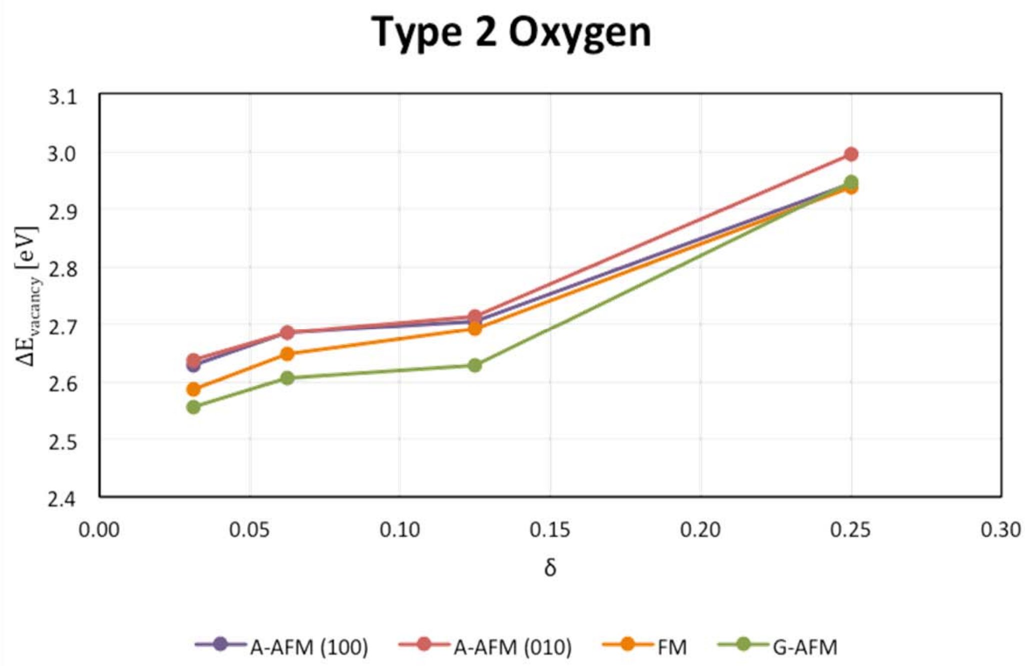


- BaMnO3 adopts antiferromagnetic configuration
- In region of infinite dilution $\Delta E_{vacancy}$ of ~ 3.2eV



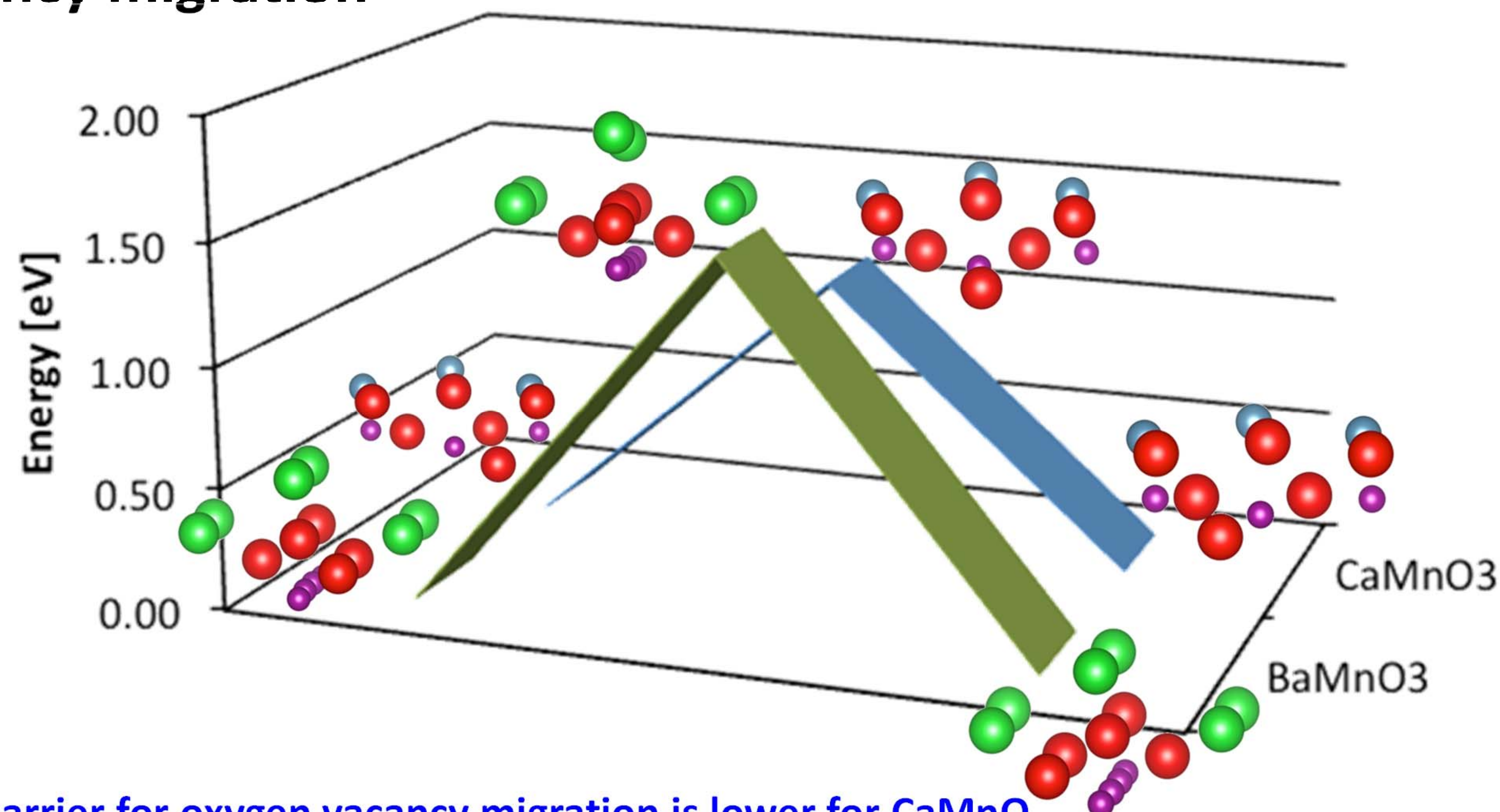
DFT Investigation: $\Delta E_{vacancy}$ (Orthorhombic $CaMnO_3$)





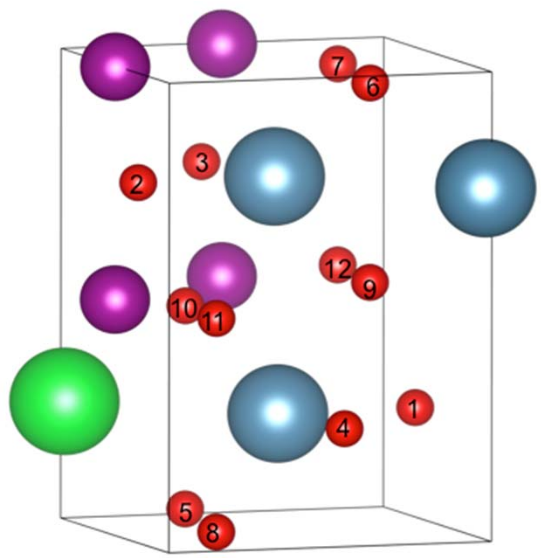
- Orthorhombic reaches a value of $\Delta E_{vacancy}$ of ~ 2.6-2.7eV
- Antiferromagnetic state is adopted
- Thermodynamically, oxygen vacancy is more favorable with $CaMnO_3$ than $BaMnO_3$

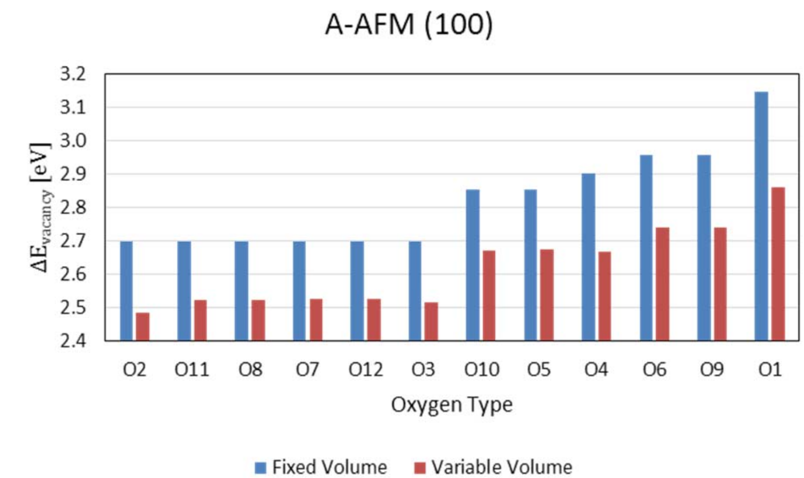
Preliminary Results: Climbing Image NEB of $E_{barrier}$ for oxygen vacancy migration

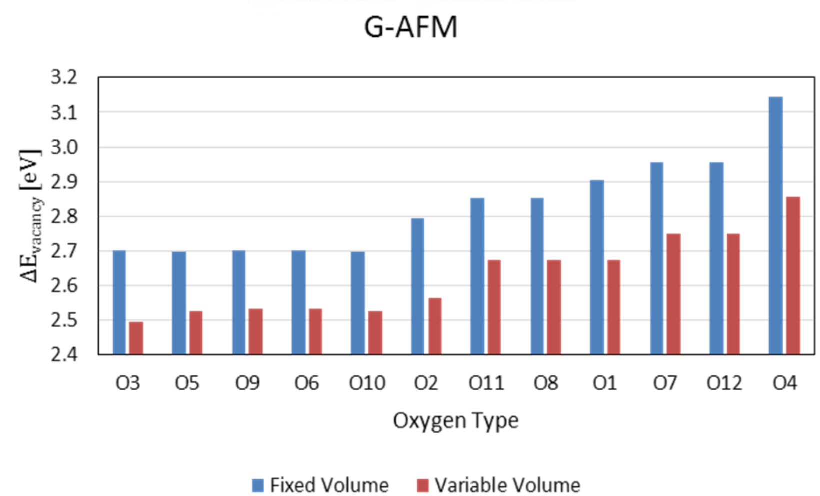


Energy barrier for oxygen vacancy migration is lower for $CaMnO_3$

$\Delta E_{vacancy}$ (Orthorhombic $Ca_{.75}Sr_{.25}MnO_3$)

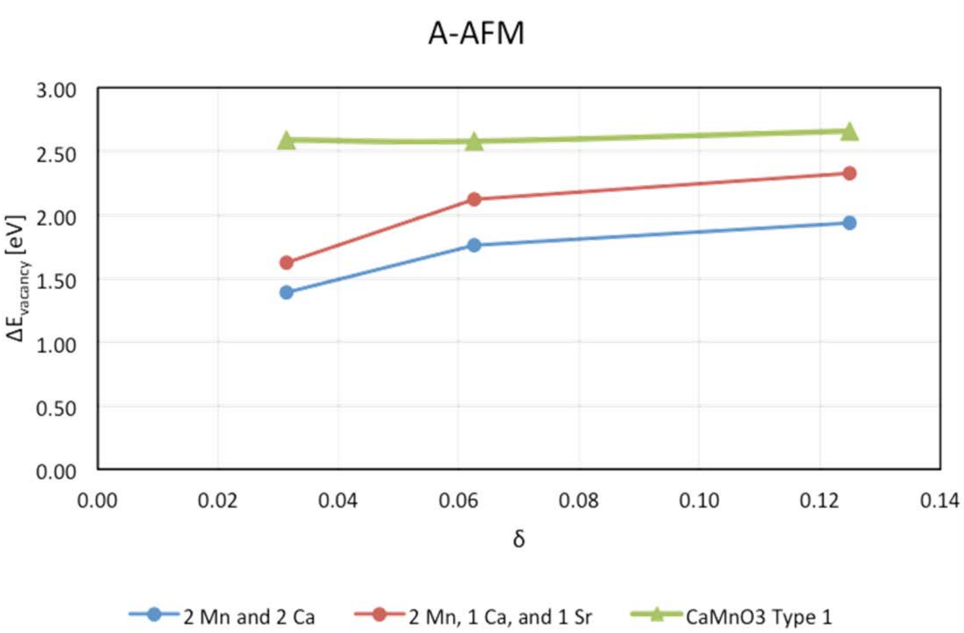


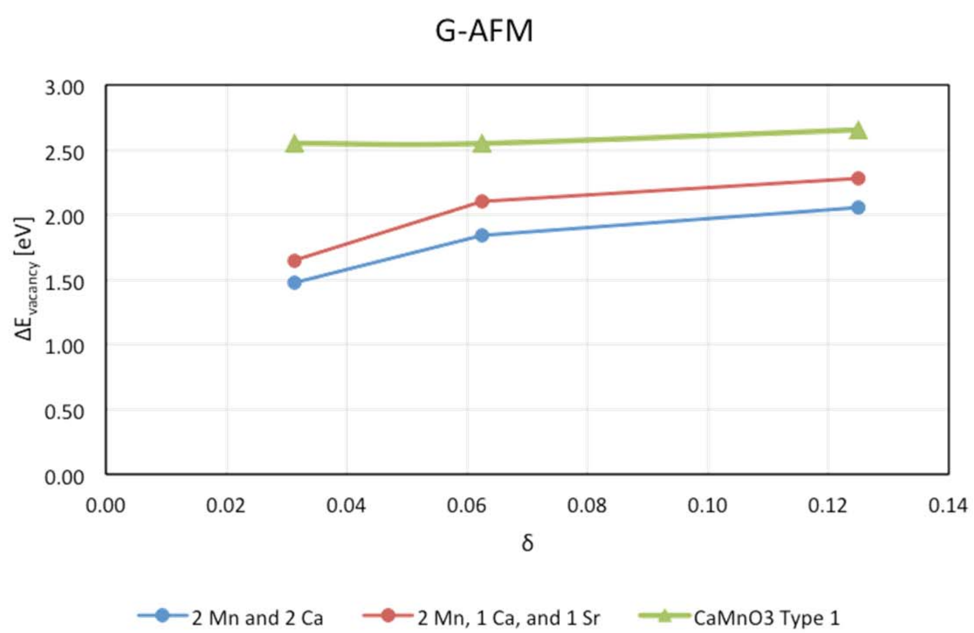




- $Ca_{.75}Sr_{.25}MnO_3$ contains 12 distinct oxygen positions
- Lower $\Delta E_{vacancy}$ with larger distance from Sr and lower coordination, e.g. smaller vacancy formation energy if O^{2-}'s closest cations being 2Mn-2Ca or 2Mn-1Sr-1 Ca

DFT Investigation: $\Delta E_{vacancy}$ (Orthorhombic $Ca_{.75}Sr_{.25}MnO_3$)





- Same trends observed for A-type and G-type antiferromagnetism
- Both magnetic states produce a $\Delta E_{vacancy}$ that is lower than $CaMnO_3$
- Sr dopant helps to promote oxygen vacancy formation

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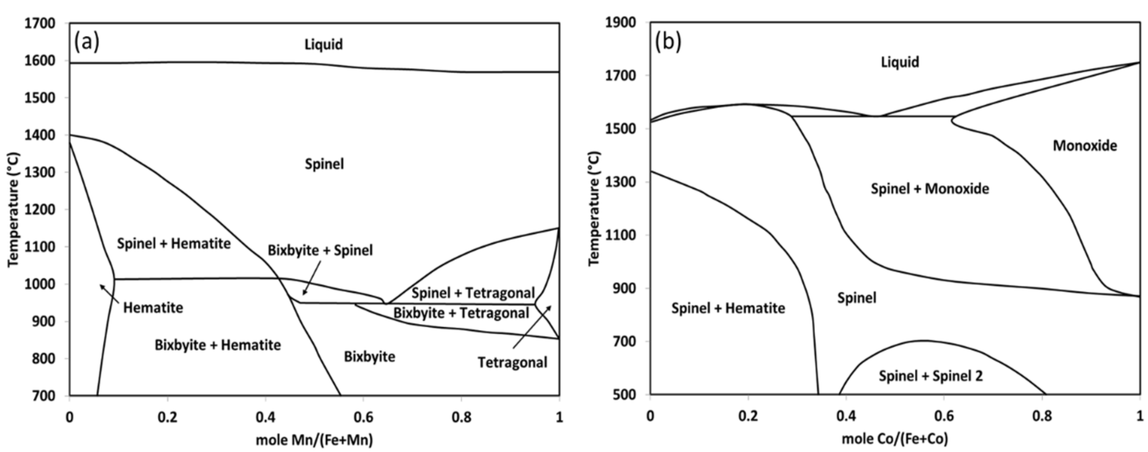
Mixed-Oxide Selection Rationale

Common CLC oxygen carriers

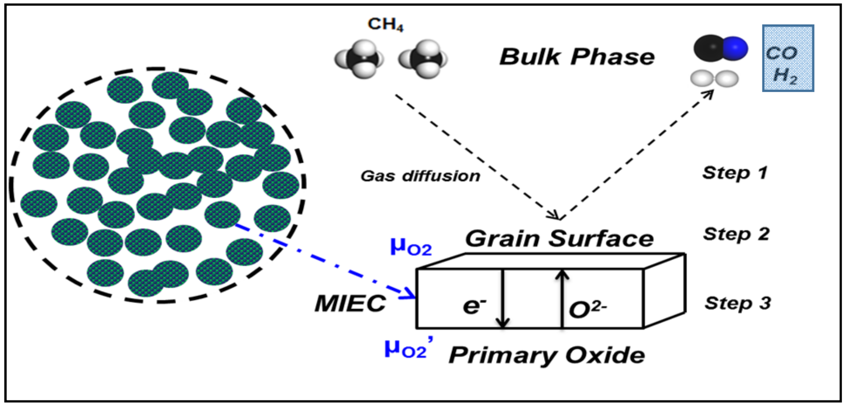
- Iron
- Copper
- Manganese
- Nickel
- Cobalt

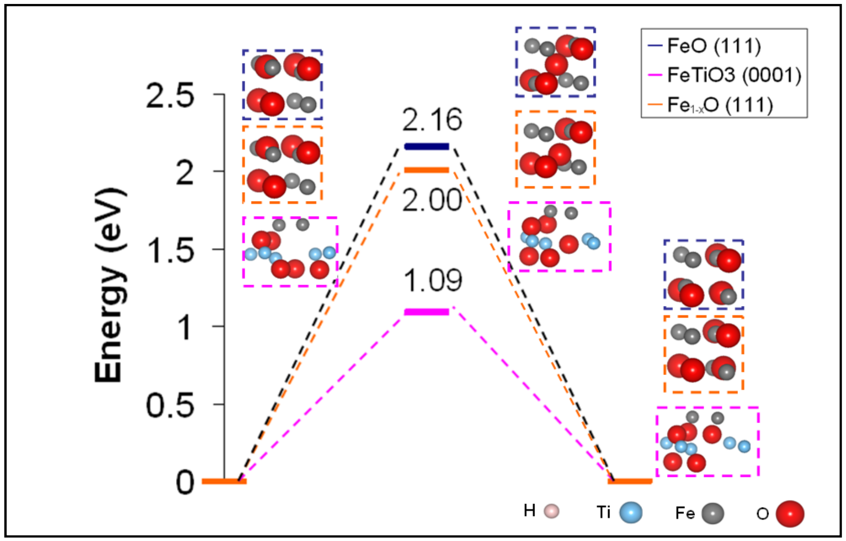
Reaction	T (°C)	ΔH (kJ/mol)	ΔG (kJ/mol)	P_{O2} (atm)
$6Fe_2O_3 = 4Fe_3O_4 + O_2$	900	493.2	145.5	3.32E-07
$6Mn_2O_3 = 4Mn_3O_4 + O_2$	900	193.1	15	0.21
$2Co_3O_4 = 6CoO + O_2$	900	406.7	11.2	0.32



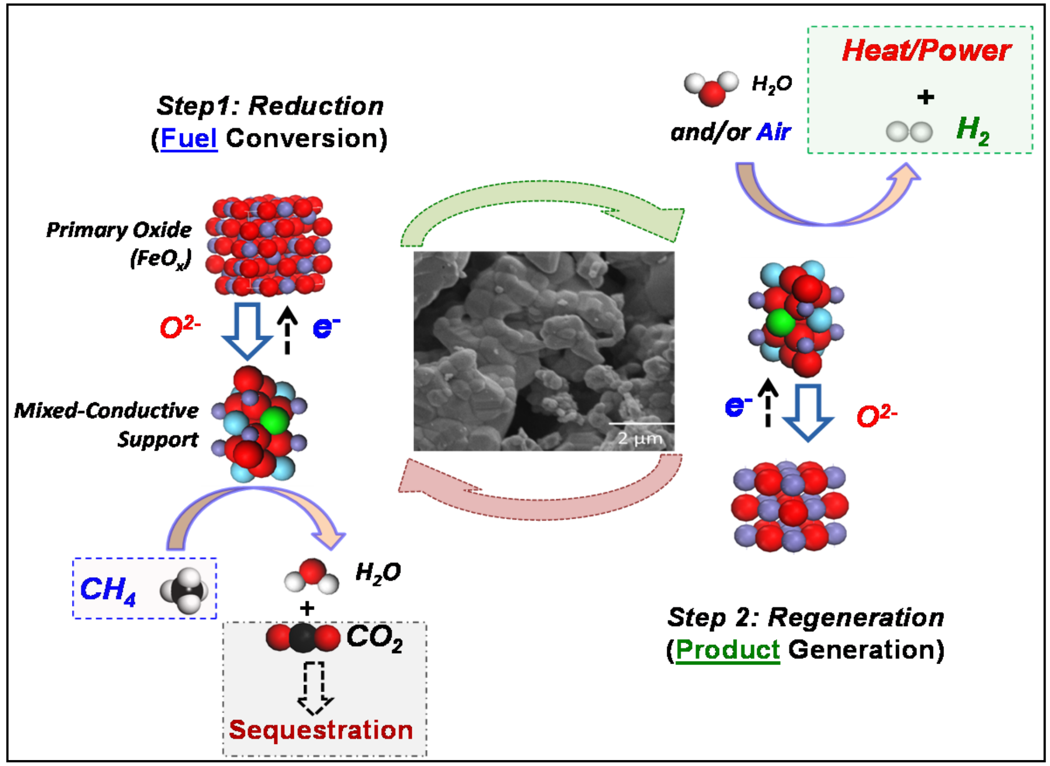
- **Samples Prepared (SSR and sol-gel methods)**
  - Iron-Cobalt mixed metal oxides
    - 30%Co-70%Fe
    - 60%Co-40%Fe
    - 90%Co-10%Fe
    - Above with LSCF support
  - Iron-Manganese mixed metal oxides
    - 50%Mn-50%Fe
    - 70%Mn-30%Fe
    - 90%Mn-10%Fe
    - Above with LSMF support

Motivation for Support Addition



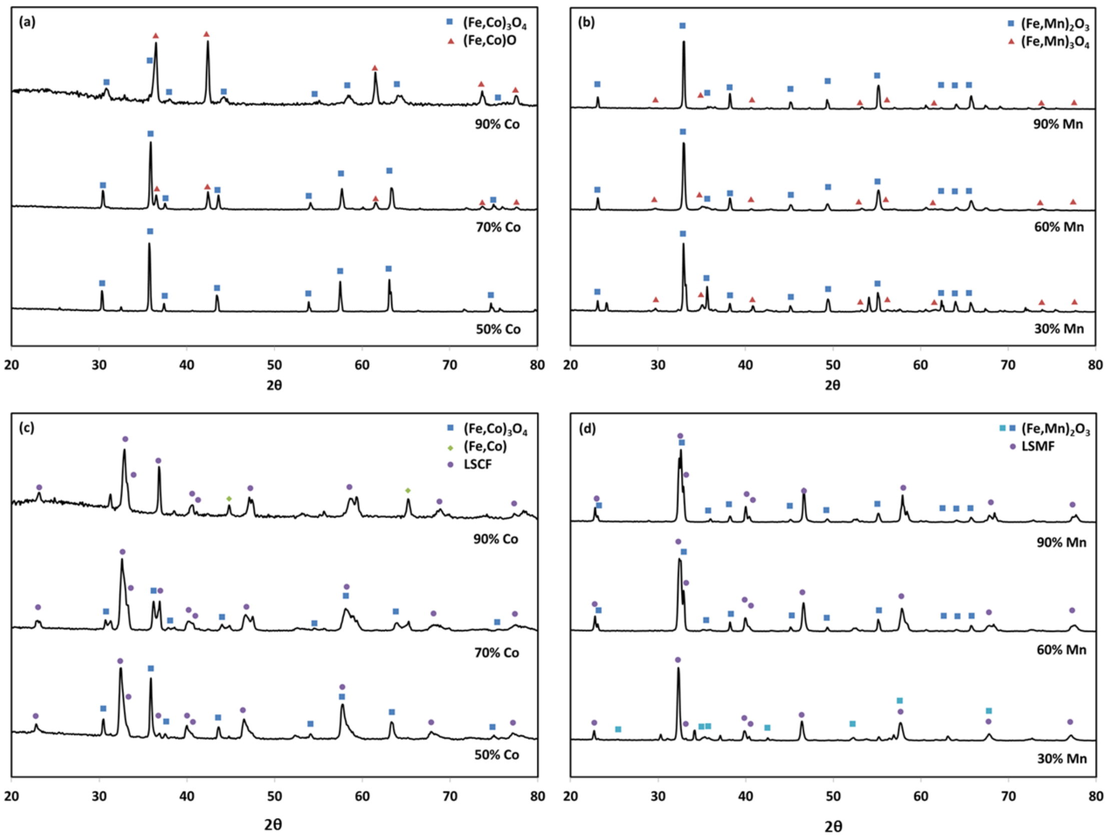


Li et al., Energy Environ. Sci., 2011, 4: 3661-3667.
Li et al., Energy Environ. Sci., 2011, 4, 876-880.



Galinsky, et al., ACS Sustainable Chem. Eng, *2013, 1, 364-373.*
Shafiefarhood et al., ChemCatChem, 2014, 6(3): 790-799.
He et al, Energy Environ. Sci., 2014, 7, 2033-2042.
Chen et al., Fuel. 2014, 134, 521-530
Shafiefarhood, et al. Fuel. 2014, DOI: 10.1016/j.fuel.2014.08.014
Neal et al., ACS Catalysis. 2014, DOI: 10.1021/cs5008415
Galinsky, et al., Applied Catalysis B: Environmental, 2015, 164, 371-379,.
He et al, Energy Environ. Sci. 2015,8, 535-539

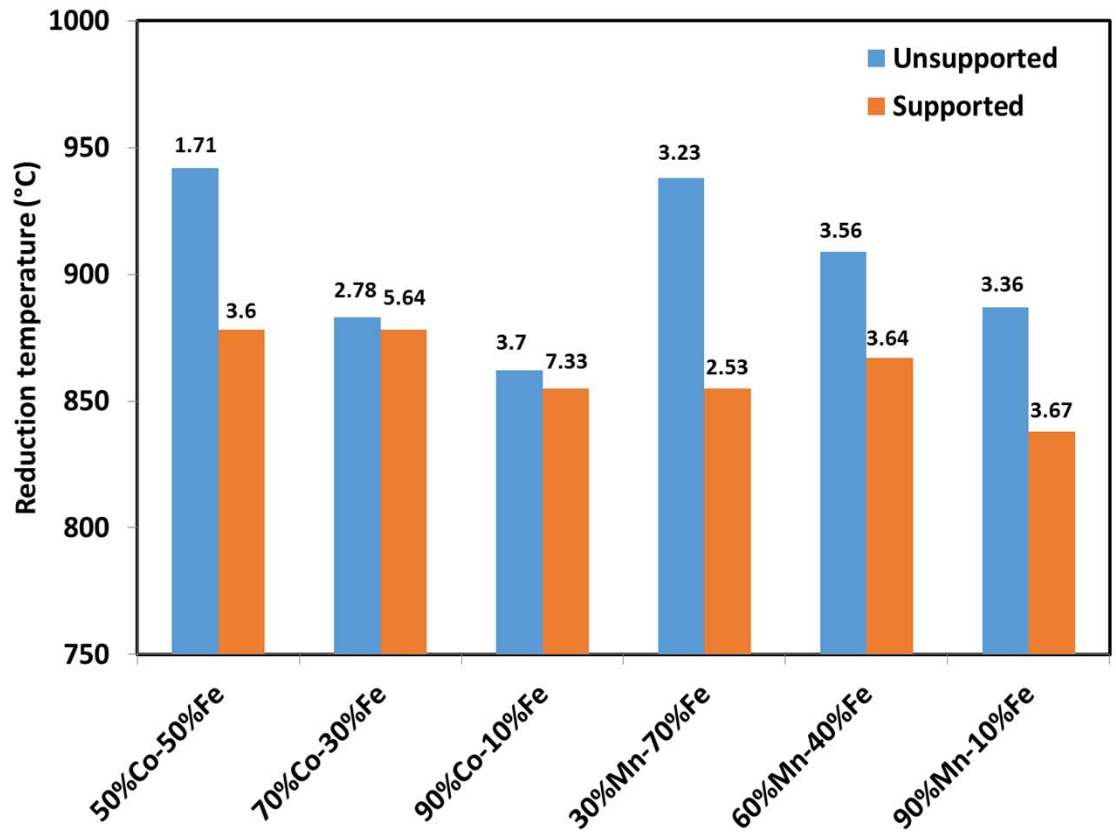
Material Synthesis and Characterizations



- XRD confirms the formation of the desired phases
- Samples with higher concentrations of Co and Mn are more prone to oxygen loss; therefore, they showed slight decomposition to lower oxidation states during sintering

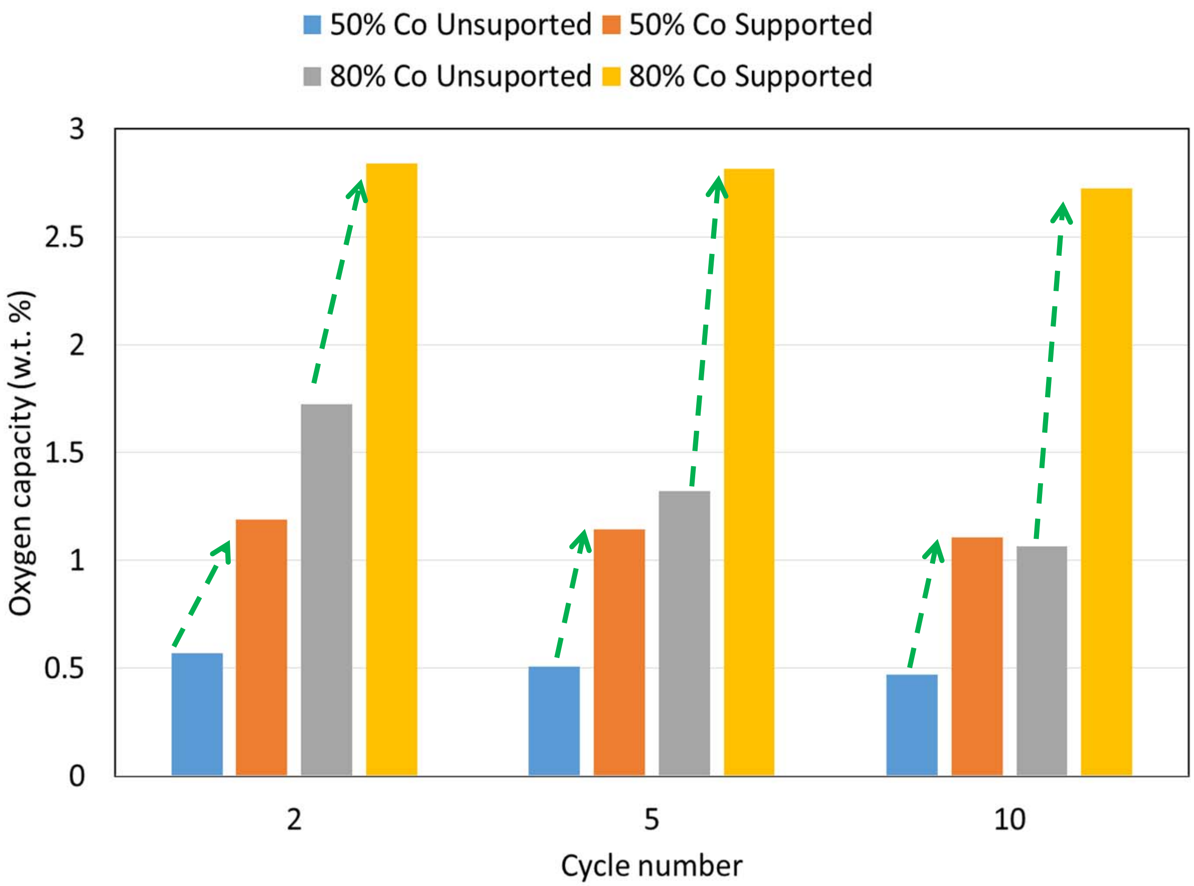
Shafiefarhood et al., Fuel. 2015, 139, 1-10

Decomposition Temperature Comparisons of Pure and Supported Samples



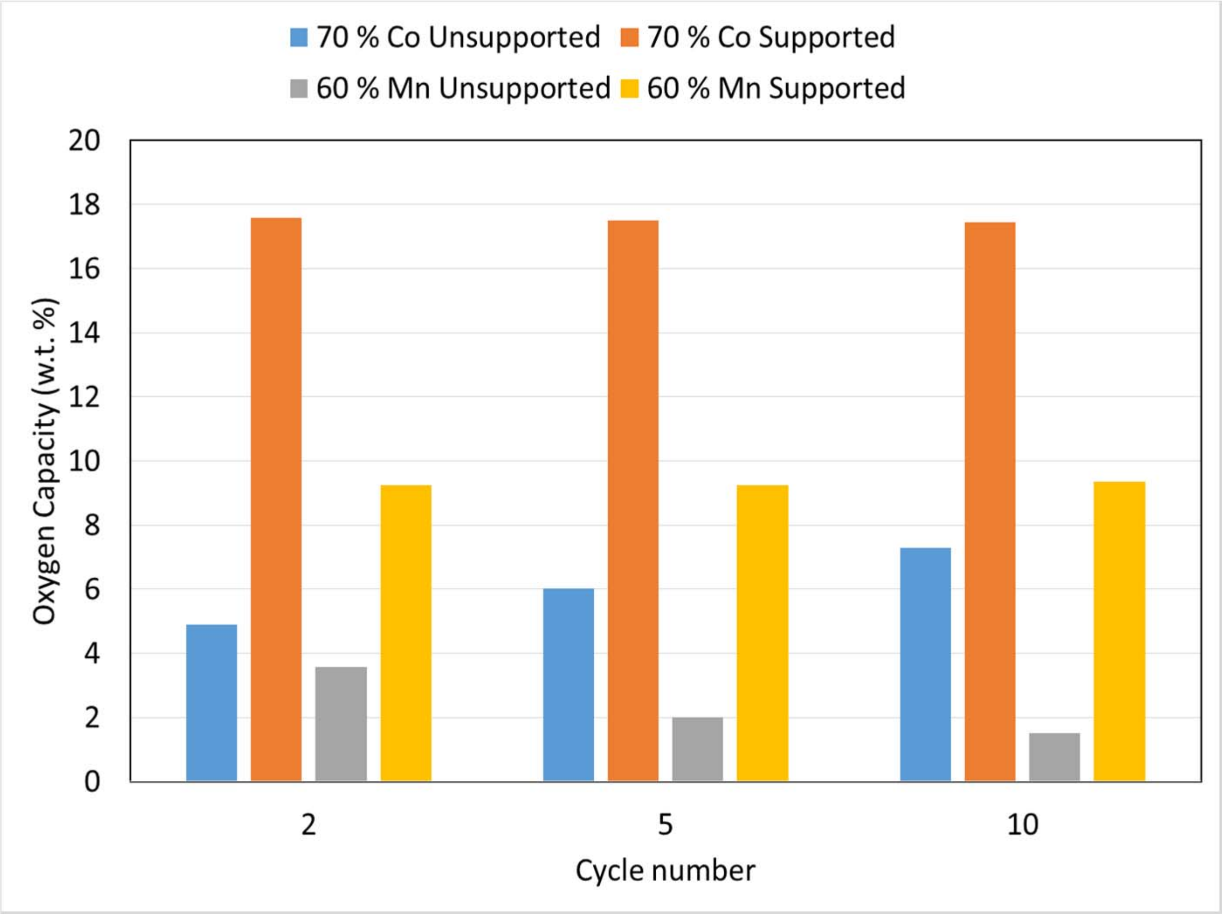
Perovskite supports reduce the decomposition temperatures of Co-Fe and Mn-Fe oxides

Isothermal CLOU Testing (850 ˚C, He inert ←→ 10% O_2)



Up to 2.9 w.t.% oxygen carrying capacity achieved, supports significantly enhances the CLOU performance of Co-Fe based oxygen carriers

Isothermal Cyclic Methane Conversion (850 ˚C, 10% CH_4 ←→ 10% O_2)



Perovskite support enhances the redox performances of both Co-Fe and Mn-Fe oxides for methane conversion

Summary

- A-site and B-site doping in $CaMnO_3$ can enhance its redox stability and low temperature CLOU properties
- DFT can be used to explain the experimental data, it can potentially be used to guide oxygen carrier development
- Mixed Mn-Fe and Co-Fe oxides can exhibit tunable redox properties
- Perovskite significantly enhances the CLOU properties of Co-Fe oxides

Future Work

- Determination of critical P_{O2} values for oxygen carrier optimization
- Comprehensive DFT calculation and validation by experimental results
- Development of effective molecular dynamic simulation tools to estimate mixed-oxide properties and use of metaheuristic algorithms for OC optimization
- Optimized OC for CLOU applications

Journal Articles

- Arya Shafiefarhood, Amy Stewart, Fanxing Li* "Iron-Containing Mixed-Oxide Composites as Oxygen Carriers for Chemical Looping with Oxygen Uncoupling (CLOU)". Fuel. 2015, 139, 1-10
- Nathan Galinsky, Amit Mishra, Jia Zhang, and Fanxing Li* "$Ca_{1-x}A_xMnO_3$ (A= Sr and Ba) Perovskite Based Oxygen Carriers for Chemical Looping with Oxygen Uncoupling (CLOU)". Applied Energy, 2015 In Press DOI:10.1016/j.apenergy.2015.04.020
- Amit Mishra and Fanxing Li "Chemical Looping Reforming of Methane Using $BaMn_{1-x}B_xO_3$ (B= Fe and Ni)" (in preparation)
- Nathan Galinsky and Fanxing Li "$CaMn_{1-x}B_xO_3$ (B=Fe, V, Ni, Co, and Al) Perovskite Based Oxygen Carriers for Chemical Looping with Oxygen Uncoupling (CLOU)" (in preparation)

Conference Presentations

- Arya Shafiefarhood, Nathan Galinsky, and Fanxing Li. "Mixed-oxides for carbonaceous fuel conversion with integrated CO_2 capture via chemical looping with oxygen uncoupling (CLOU)" 248th ACS National Meeting. San Francisco, CA. August 2014.
- Arya Shafiefarhood, Nathan Galinsky, Amit Mishra, and Fanxing Li. "Composite mixed oxides for chemical looping with oxygen uncoupling." 3rd International Conference on Chemical Looping. Gothenburg, Sweden. 10 September 2014. Conference Presentation.
- Nathan Galinsky, Amit Mishra, and Fanxing Li. "Perovskite Based Oxygen Carriers for Chemical Looping with Oxygen Uncoupling." 2014 AICHE Annual Meeting. Atlanta, GA. 19 November 2014.

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  - Nathan Galinsky
  - Arya Shafiefarhood
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Thanks!

DFT Parameters

VASP package

Electron Ion Interaction: PAW

Exchange correlation functional: PBE-GGA

Energy cut-off: 425 eV

EDIFF = 10^{-4} eV

Fixed mesh density for varying super cell sizes:

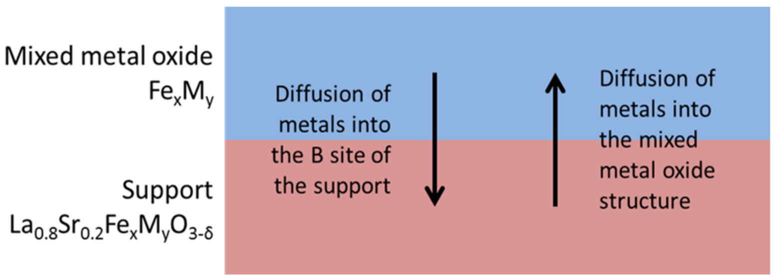
Orthorhombic CaMnO3: 4x4x4 for 1 unit cell; monkhorst pack

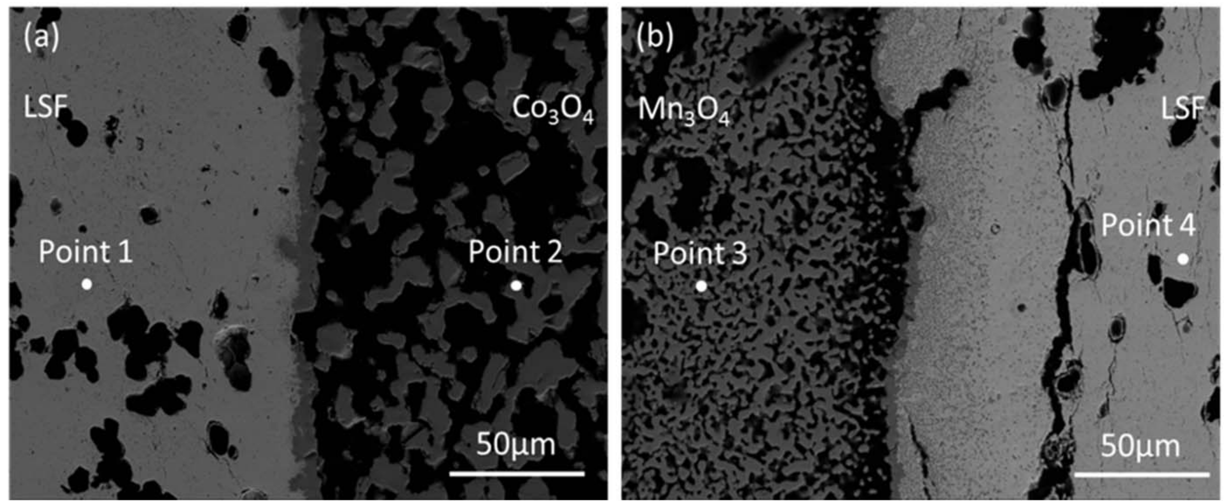
Orthorhombic Ca.75Sr.25MnO3: 4x4x4 for 1 unit cell; monkhorst pack

Hexagonal BaMnO3: 4x4x4 for 1 unit cell; Gamma centered

$$E_{O_V} = E_{AMnO_{3-\delta}} + \frac{1}{2} E_{O_2} - E_{AMnO_3}$$

Spinel/Bixbyite – Perovskite Phase Compatibility Studies



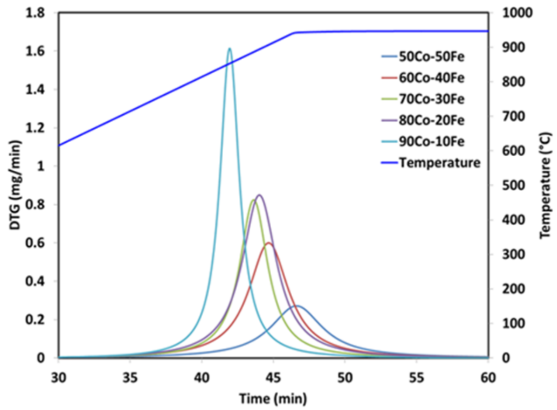


- ***Sharp concentration differences when passing the phase boundary confirms that no significant phase diffusion is occurred and Co tends to stay in the mixed metal oxide part***
- ***Gradual decrease in concentration of Mn when passing the phase boundary implies that manganese diffused through the LSF support and substitute iron in its B-site***

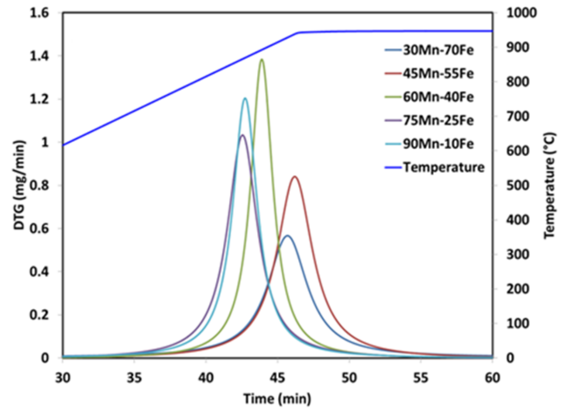
Element	**Atomic % from EDX**			
	Point 1	Point 2	Point 3	Point 4
Co or Mn	2.39	98.80	99.50	4.64
Fe	60.55	1.13	0.46	57.93
La	29.07	0.01	0.00	27.36
Sr	7.99	0.06	0.03	10.06

Metal Oxide Decomposition Behavior

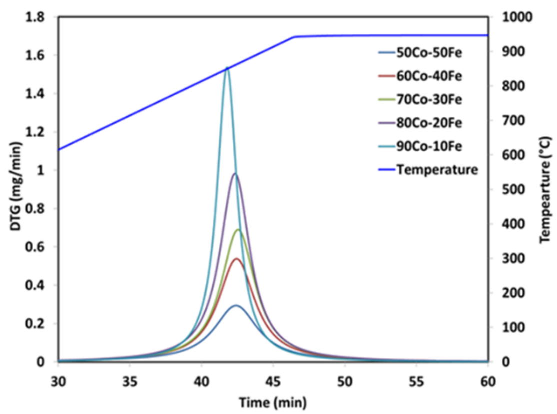
Co-Fe oxide



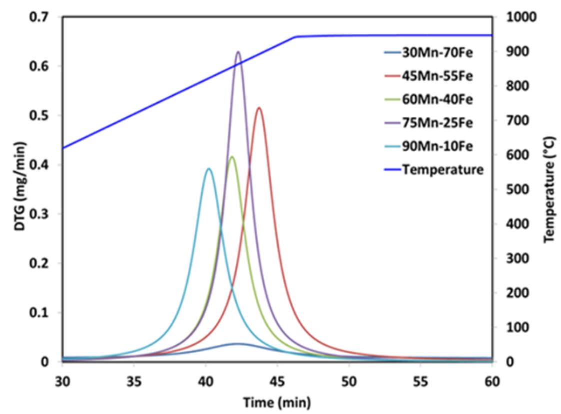
Mn-Fe oxide



Co-Fe oxide + LSCF Support



Mn-Fe oxide + LSMF Support



Decomposition temperature of Co-Fe and Mn-Fe oxides decrease with decreasing Fe content.
Supported samples do not exhibit clear trends.

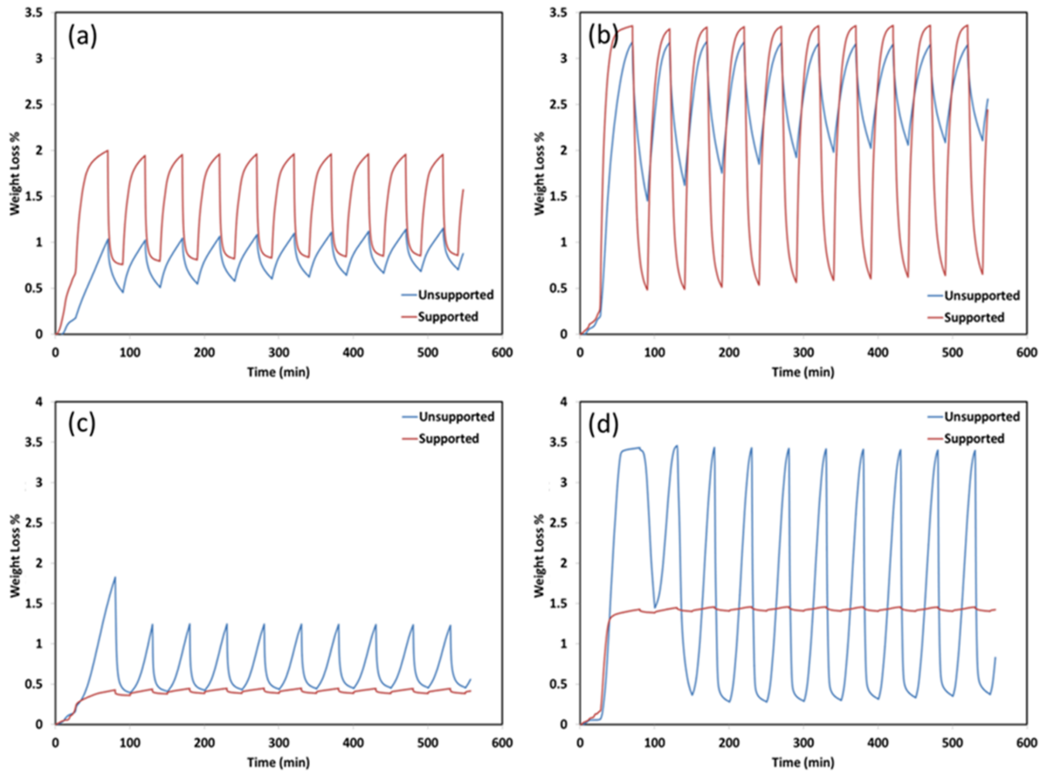
Isothermal CLOU Testing (850 ˚C, He inert ←→ 10% O_2)

50% Co – 50% Fe

80% Co – 20% Fe

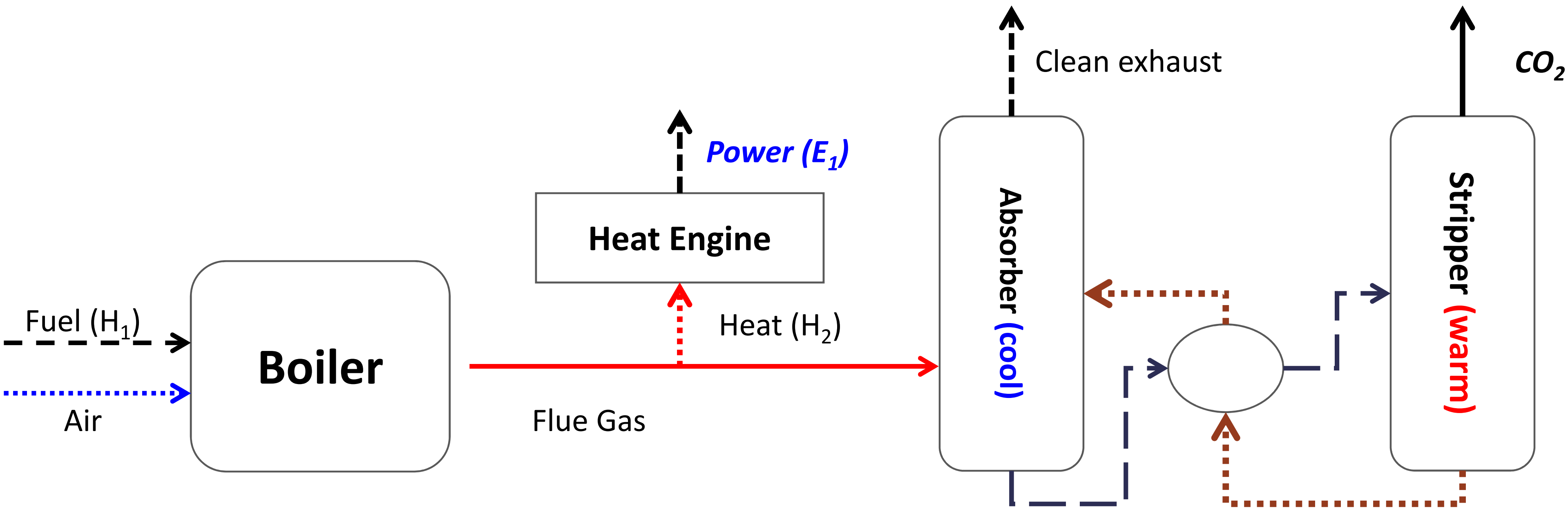
30% Mn – 70% Fe

60% Mn – 40% Fe



- ***CLOU properties of mixed Fe-Co oxides are enhanced by perovskite addition***
- ***Oxygen carrying capacity of mixed Fe-Mn oxides under an isothermal condition is negatively affected by perovskite addition***

Why Chemical Looping: Conventional Post-Combustion CO_2 Capture

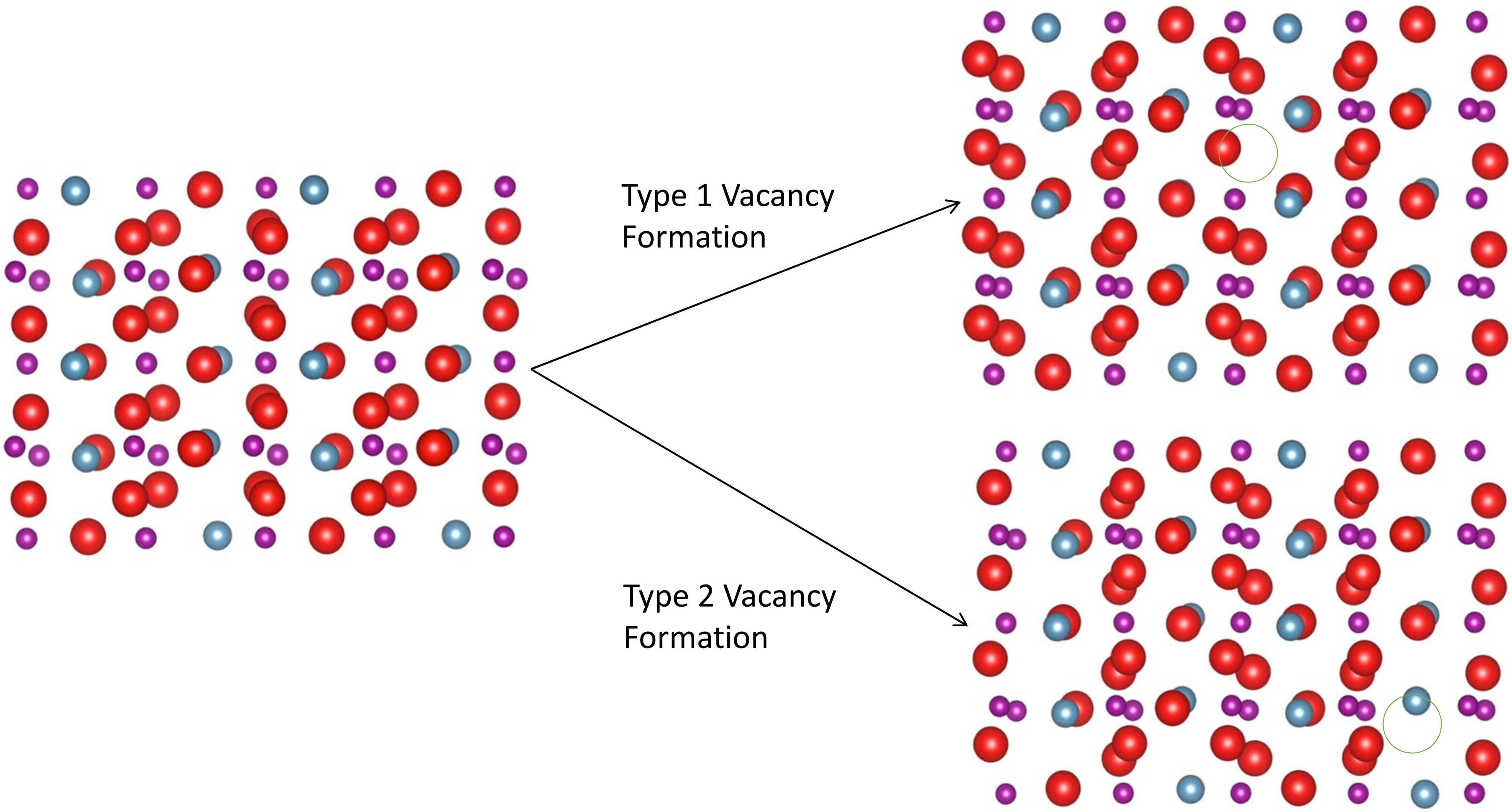


Limitations to conventional combustion – absorption based processes:

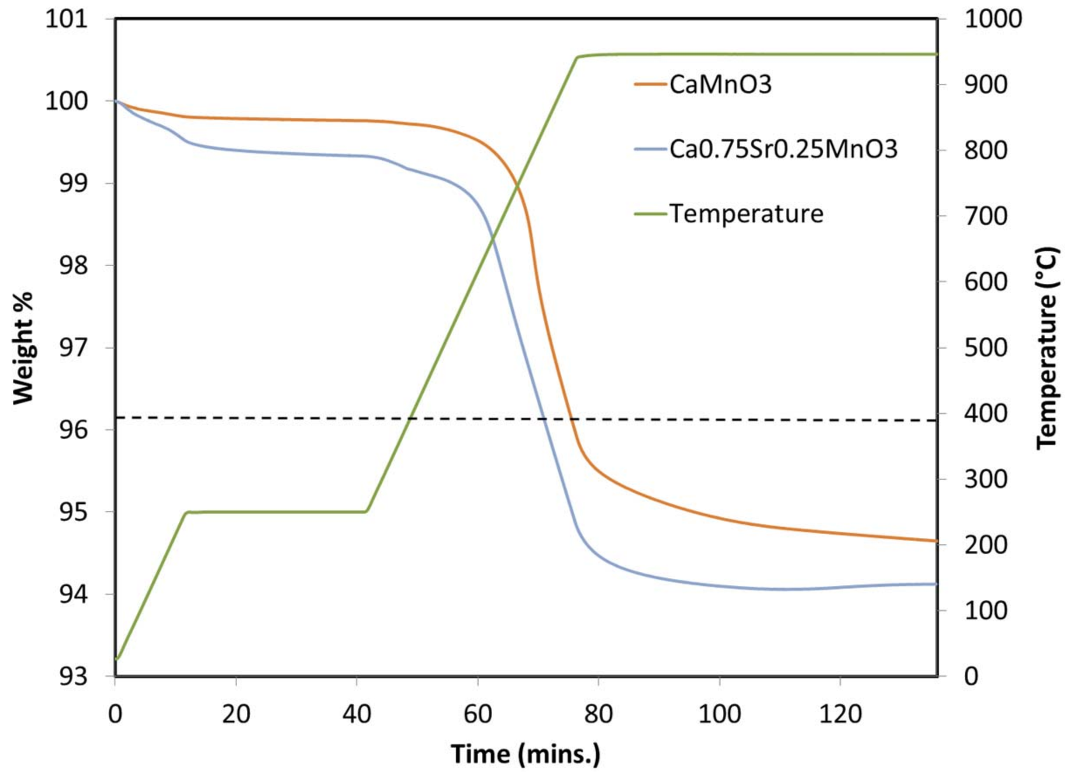
- **Fixed extractible enthalpy from boiler/flue gas**
- **Absorber-stripper cycle consumes high grade heat and rejects low grade heat**
- **Delivery pressure of CO_2 is limited**

Low 2nd Law efficiency!

DFT Investigation: $\Delta E_{vacancy}$ (Orthorhombic $CaMnO_3$)



Char Oxidation using Perovskites



Sr doped perovskite shows notably lower reaction temperatures for char oxidation