SAND2017-6796C

Calcium Manganite-Based Materials for High Temperature CSP Thermochemical Energy Storage

Andrea Ambrosini

Sandia National Labs

Sean Babiniec, Eric Coker,
James E. Miller

Solid State Ionics 21
Padova, Italia
21 June 2017

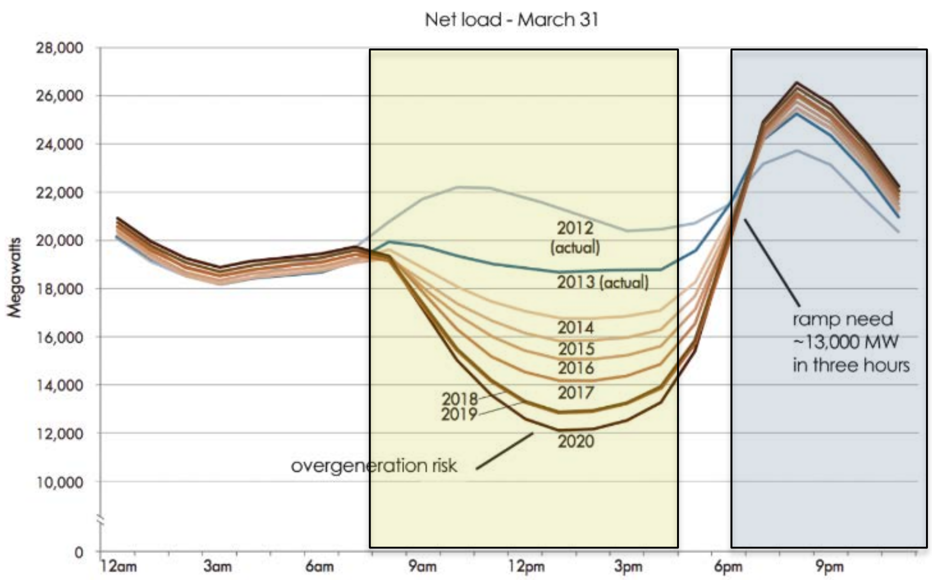
SunShot U.S. Department of Energy

Sandia National Laboratories

Motivation

Intermittent, diurnal nature requires energy storage

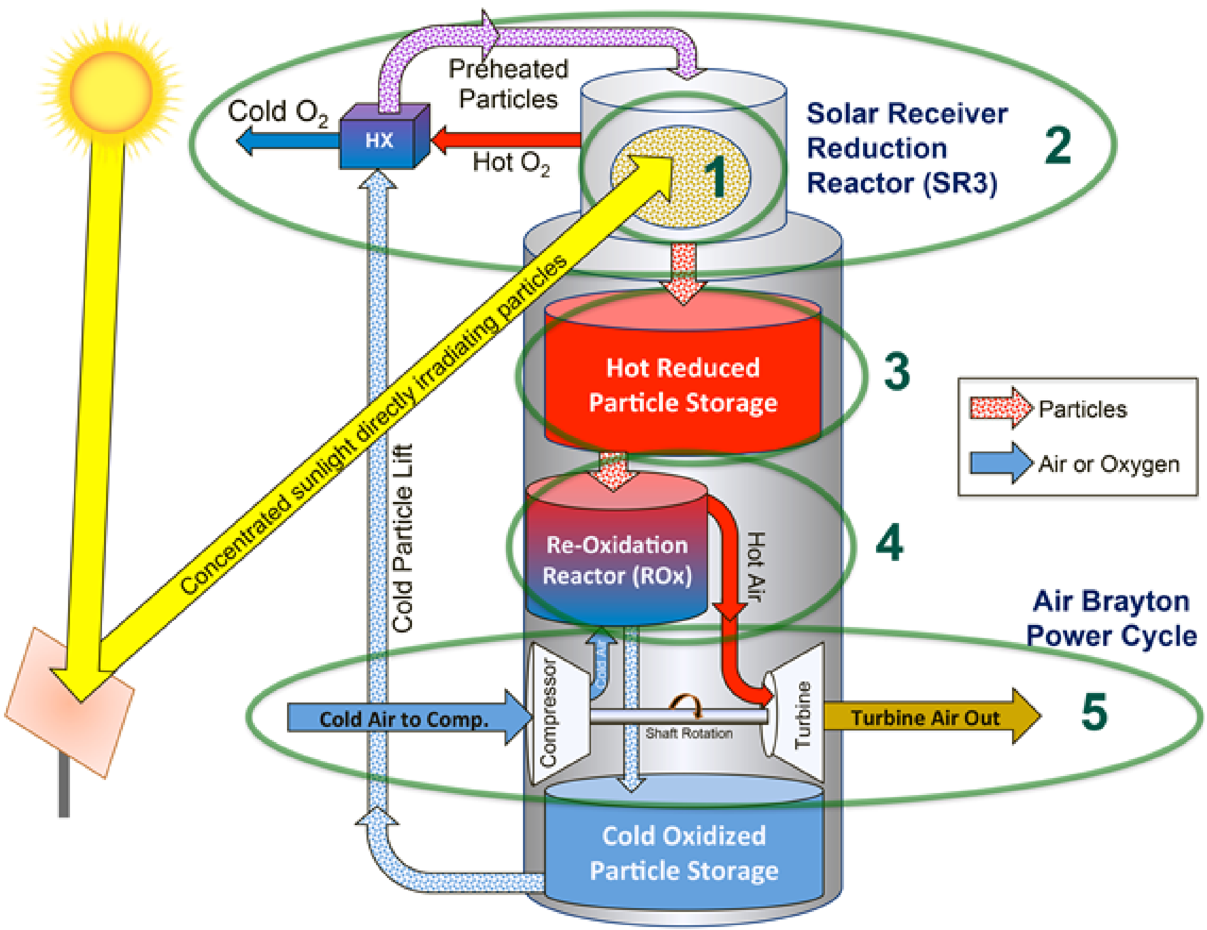
- Increase the duration of electricity generation
- Shift the period of operation to peak demand



Enabling technologies are needed to store and deliver thermal energy to high-temperature (> 1000 °C), high-efficiency power cycles, e.g., Air Brayton. The technology must be low cost ($15/kWh$_{th}$), which demands high energy density solutions.

PROMOTES

High Performance Reduction/Oxidation Metal Oxides for Thermochemical Energy Storage



1. Materials Enabled Innovation ($\Delta H_{total} \geq 1500$ kJ/kg)
2. Solar Receiver Reduction Reactor
3. Particle Storage at T > 1000 ºC
4. Pressurized oxidation reactor Air acts as reactant and heat transfer fluid. Open cycle – no gas storage.
5. High Temp/High Efficiency Air Brayton Power Cycle.

Thermochemical Energy Storage

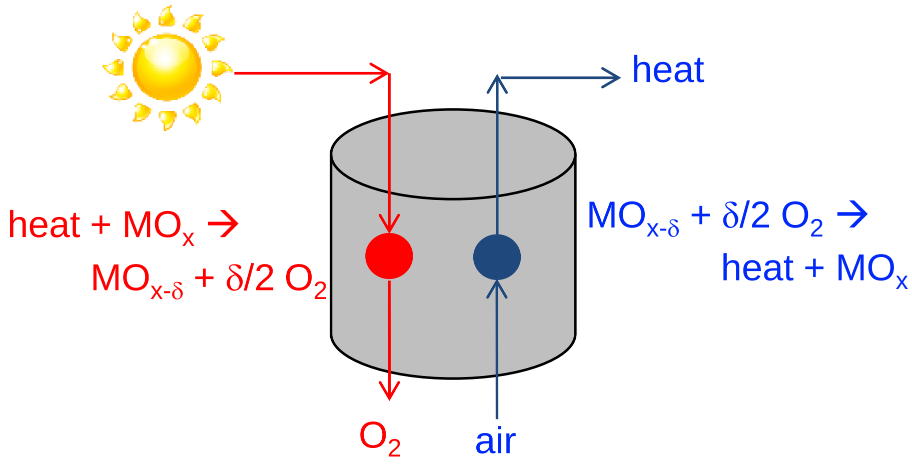
Redox-active metal oxides are ideal materials for storage in high temperature cycles

Materials Concept:

- Leverage both *sensible heat and heat of reaction* for energy storage
- Demonstrate chemical and physical stability at extreme temperatures
- Operate over a broad range of temperatures and pressures
- Develop and tailor materials properties through elegant design and manipulation of metal oxide chemistry

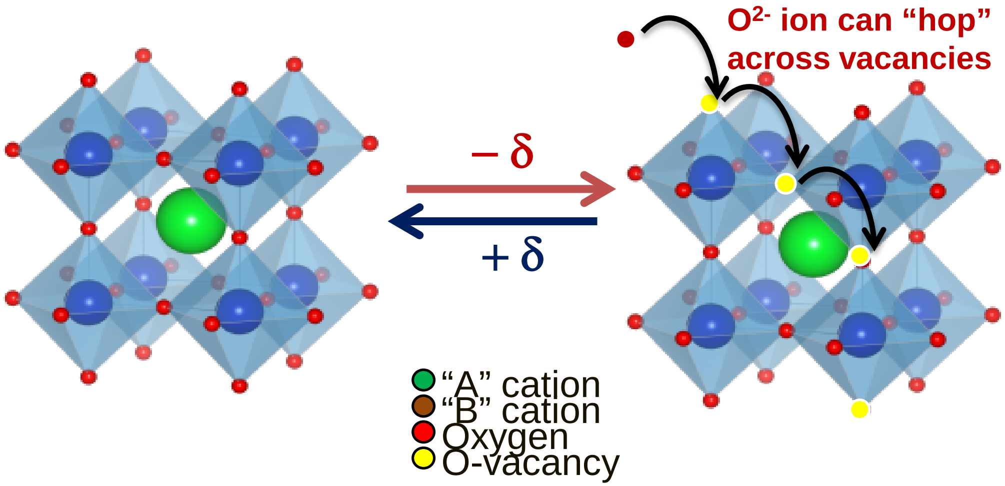
Advantages of Metal Oxides (MO):

- Open or closed configurations
- Air can act as both the reactant and heat transfer fluid
- Environmentally benign
- No catalyst necessary
- No compression required for storage
- Amenable to multiple scales and temperature ranges



Mixed Ionic-Conducting (MIEC) Oxides

- Redox-active materials which efficiently conduct both O^{2-} and electrons
- No crystallographic phase change occurs during redox
- Vacancies facilitate oxide ion transport
- Redox activity continuous over variety of T and pO_2



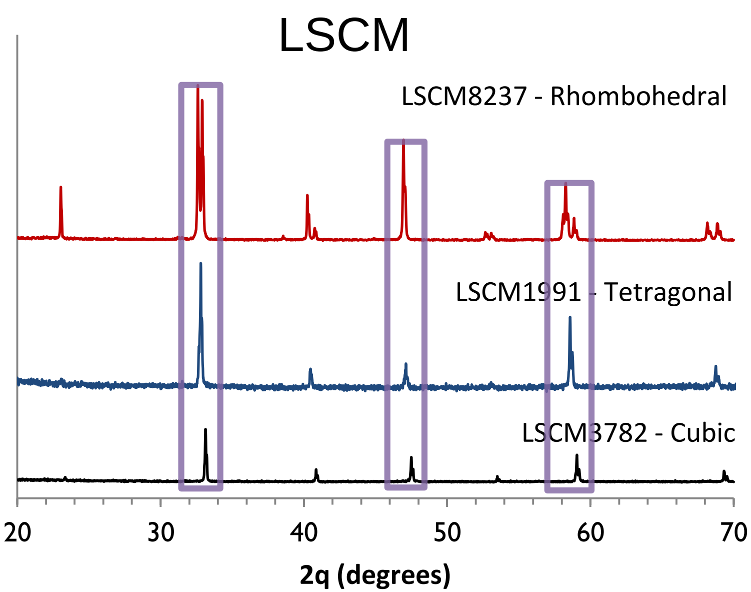
Parameter Space:

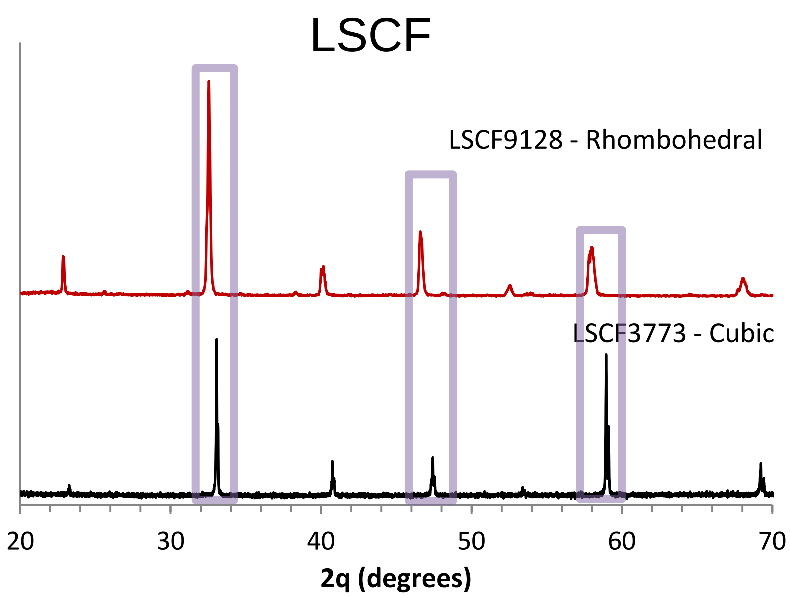
- Energy storage capacity, $\Delta H_{tot} = \Delta H_{rxn} + C_p\Delta T = 1500$ kJ/kg
- Cycling between T_H of 1000 – 1350 °C and T_L of 200 °C
- pO_2 during reduction $\geq 10^{-3}$ atm
- pO_2 during oxidation ≤ 1 atm

Doped $LaCoO_3$

$La_xSr_{1-x}Co_yMn_{1-y}O_{3-\delta}$ (LSCM) and $La_xSr_{1-x}Co_yFe_{1-y}$ (LSCF)

- Known redox-active perovskite materials
- Large solid solubility range
- Crystallize in several perovskite-related space groups
- In general: more symmetric space groups show higher redox capacities



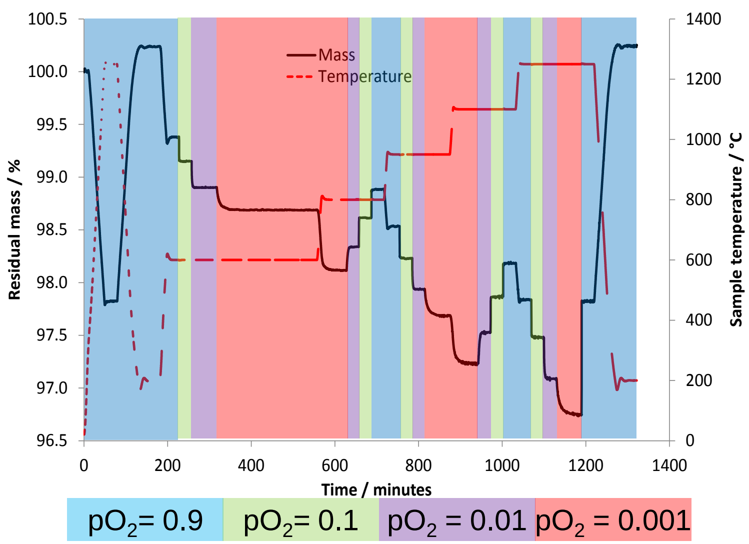


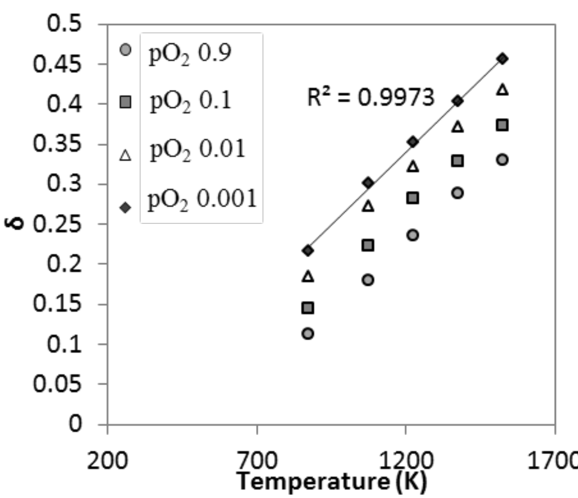
High-Resolution Equilibrium TGA

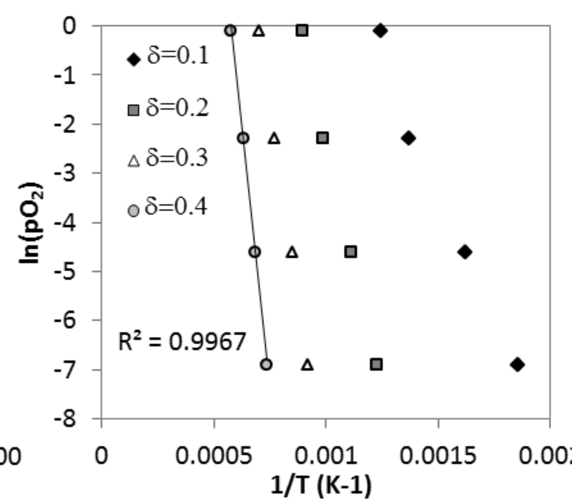
- Used to estimate thermodynamic parameters
- Isothermal holds at 600, 800, 950, 1100, and 1250 °C; pO_2 varied at each temperature and held until equilibrium
- Thermodynamic parameters extracted by van't Hoff approach:

$$\ln(pO_2) = 2\frac{-\Delta G_{rxn}}{RT} = 2\left(\frac{1}{T}\cdot\frac{-\Delta H_{rxn}}{R} + \frac{\Delta S_{rxn}}{R}\right)$$

- Enthalpy determined by slope, entropy by intercept for each value of δ





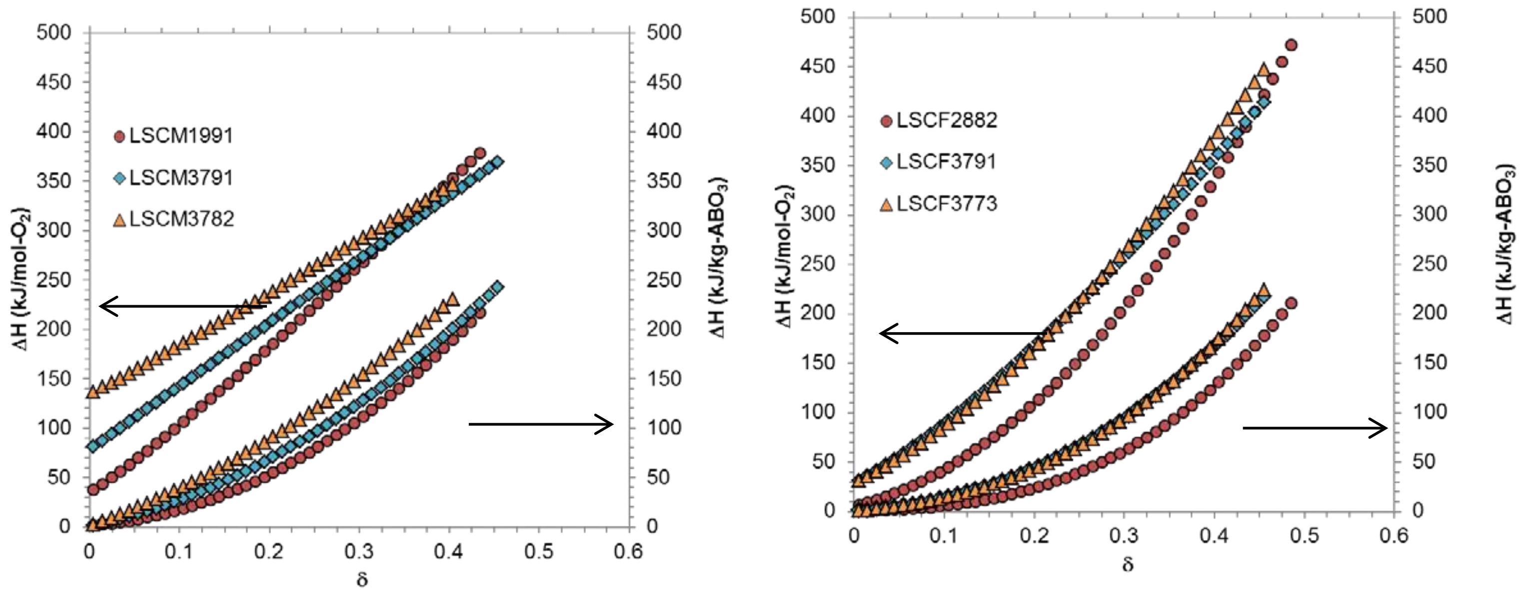


SunShot U.S. Department of Energy

Sandia National Laboratories

LSXM Enthalpy

- Partial molar: describes energy to remove a mole of O_2 at a specific δ
- Enthalpies must be integrated over δ to describe continuous reaction by series of discrete reactions

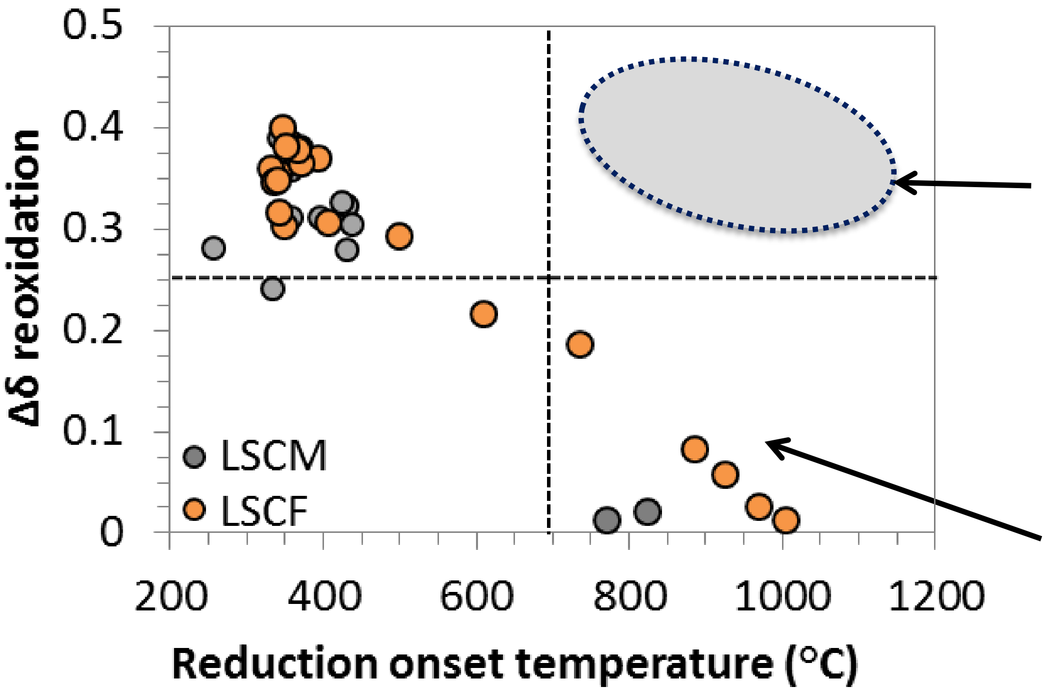


Material	Reduction onset (°C)	Maximum δ	Enthalpy at δ_{max} (kJ/kg)
LSCM1991	432	0.434	216
LSCM3791	343	0.460	242
LSCM3782	359	0.412	236
LSCF2882	357	0.486	212
LSCF3791	352	0.461	223
LSCF3773	348	0.455	223

Increasing Reaction Enthalpy

$$\Delta G_{red} = \Delta H_{red} - T\Delta S_{red}$$

- $\Delta G_{red} = 0$ is the onset of reduction (equilibrium)
  - Assuming entropy term is similar between materials (i.e., constant), a change in reduction enthalpy necessitates a change in reduction temperature



Ideal materials show a favorable balance of increased reduction onset temperature without large decrease in reduction capacity. New compositions focus on materials in this window.

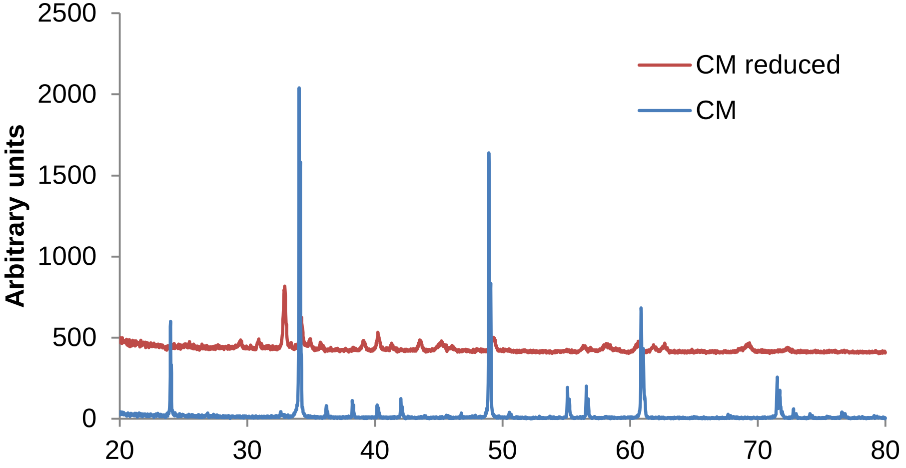
In the LSCX system, materials with high reduction temperatures had low redox capacity ($\delta < 0.25$).

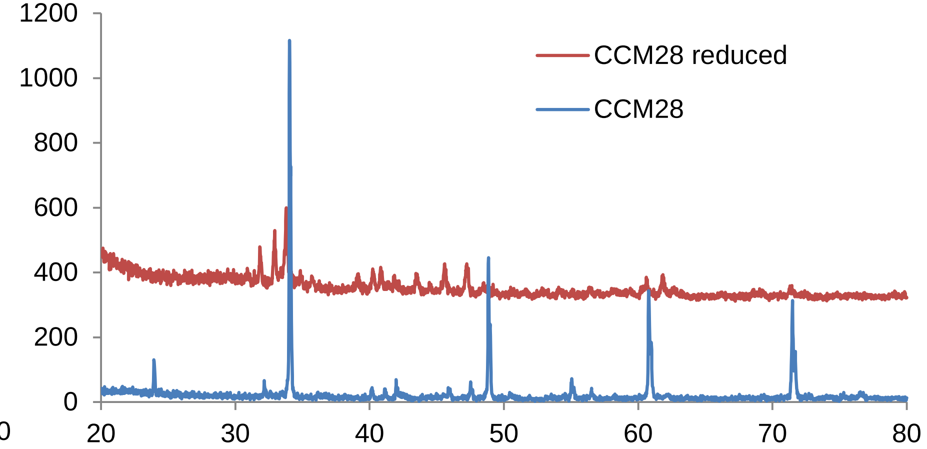
Doped $CaMn_{1-y}B_yO_{3-\delta}$ Perovskites

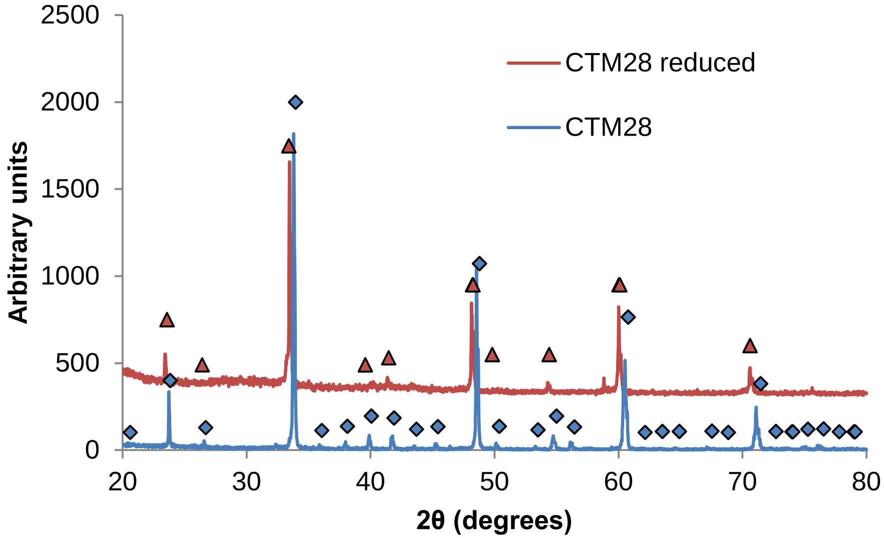
- Ca is a +2 element, forcing the B-site, e.g. Mn, to adopt a higher oxidation state (+4)
- Ca as the main element in the A-site lowers the molecular weight dramatically (Ca = 40.078 g/mol)
- Ca more abundant and less expensive than Sr or La
- Calcium-based perovskites reduce at high temperatures,
  - Higher reduction temperatures indicative of stronger M-O bonds, resulting in increased partial molar reduction enthalpies
- T_{red} of $CaMnO_3$ = 875 °C (vs. 432 °C for LSCM1991)
  - However, decomposes under reducing conditions
  - Doping CMO can help stabilize the structure

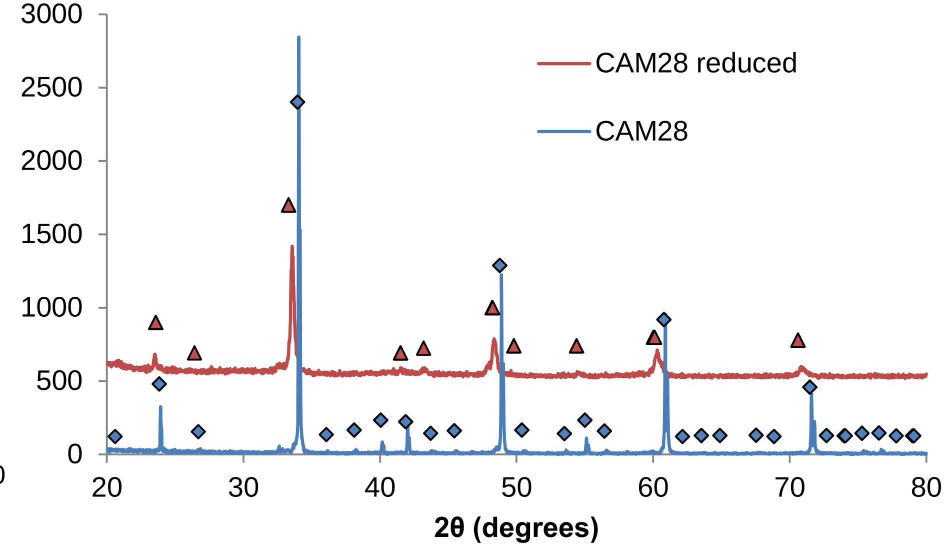
Stability Under Reducing Conditions

- CCM28 and CM decompose under 1000 ^{o}C Ar anneal
- CTM28 and CAM28 convert from orthorhombic (blue) to tetragonal (red)









SunShot U.S. Department of Energy

Sandia National Laboratories

Total Storage Potential

$$\Delta H_{tot} = \Delta H_{rxn} + C_p \Delta T$$

Latent heat assumes pO_2 swing of 0.001 to 0.9
Sensible heat assumes Cp = 15R, T_L = 200 °C

LSCM3791

Temperature (°C)	Sensible (kJ/kg)	Latent (kJ/kg)	Total (kJ/kg)
1100	536	192	728
1200	595	225	820
1350*	684	289*	973

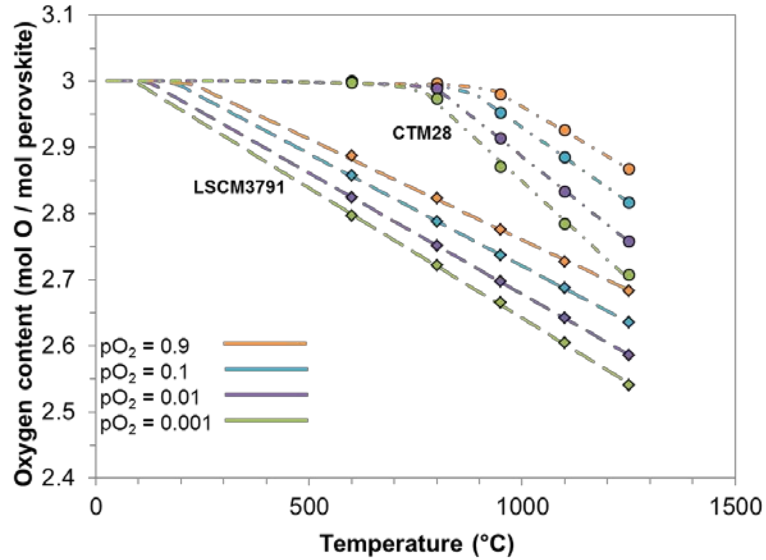
CTM28

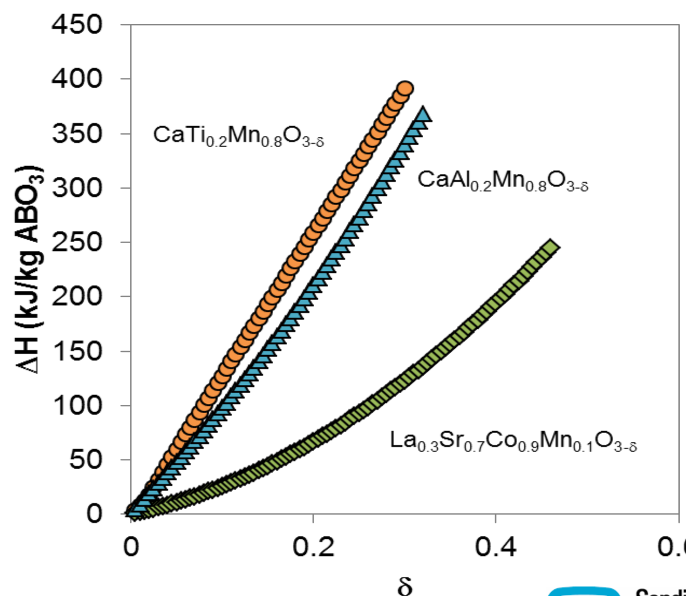
Temperature (°C)	Sensible (kJ/kg)	Latent (kJ/kg)	Total (kJ/kg)
1100	793	290	1083
1200	881	362	1243
1350*	1013	481*	1494

CAM28

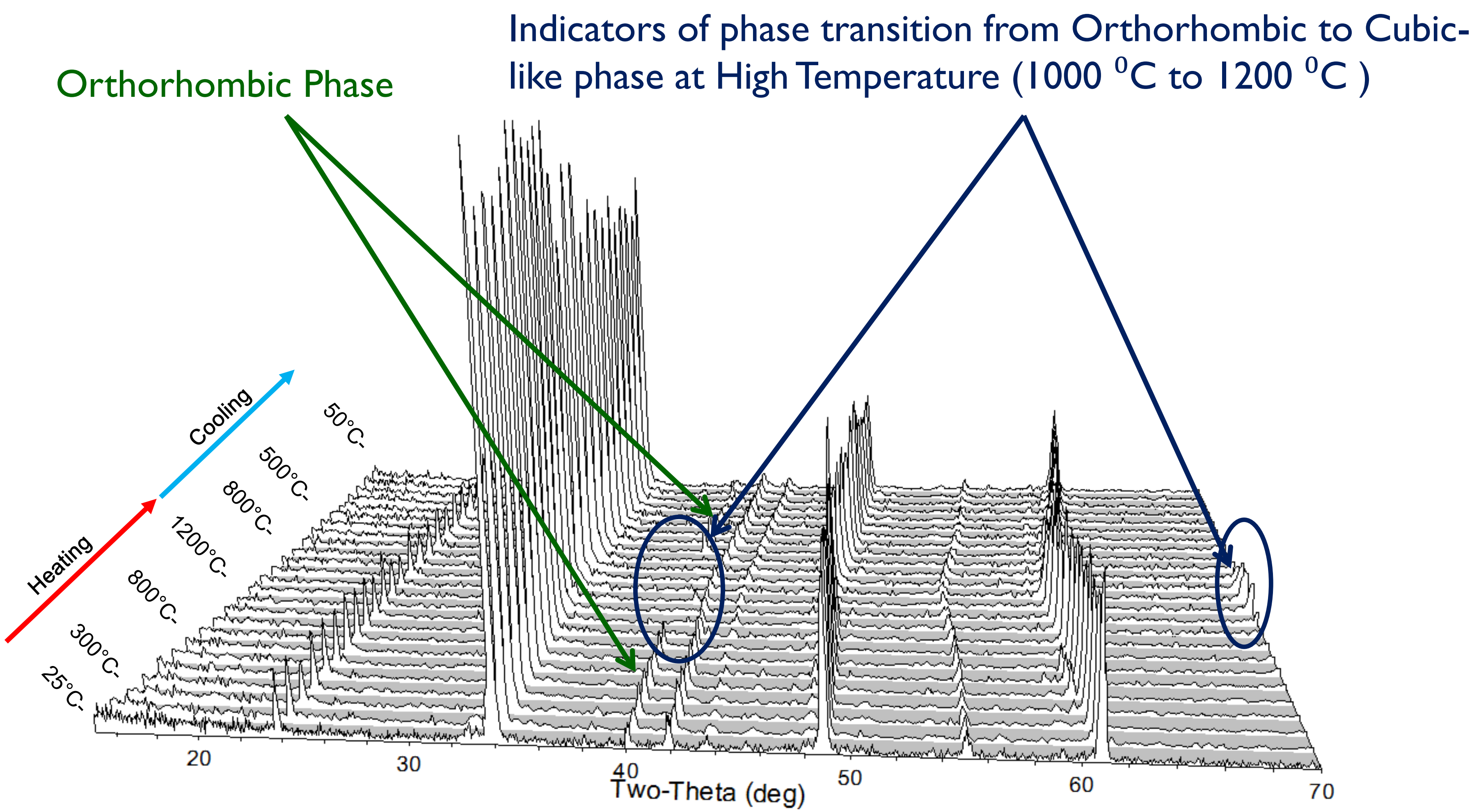
Temperature (°C)	Sensible (kJ/kg)	Latent (kJ/kg)	Total (kJ/kg)
1100	826	293	1119
1200	918	351	1269
1350*	1056	450*	1506

*Values at 1350 °C are extrapolated from δ vs T data





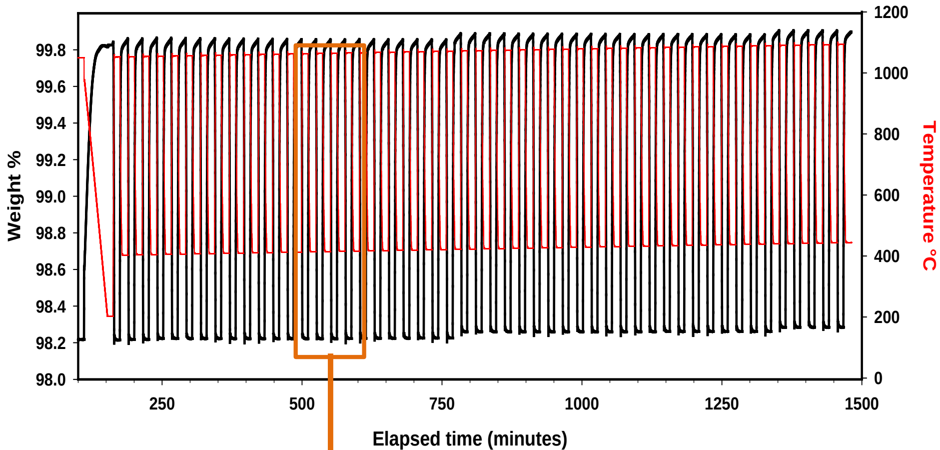
CAM28 In-situ XRD

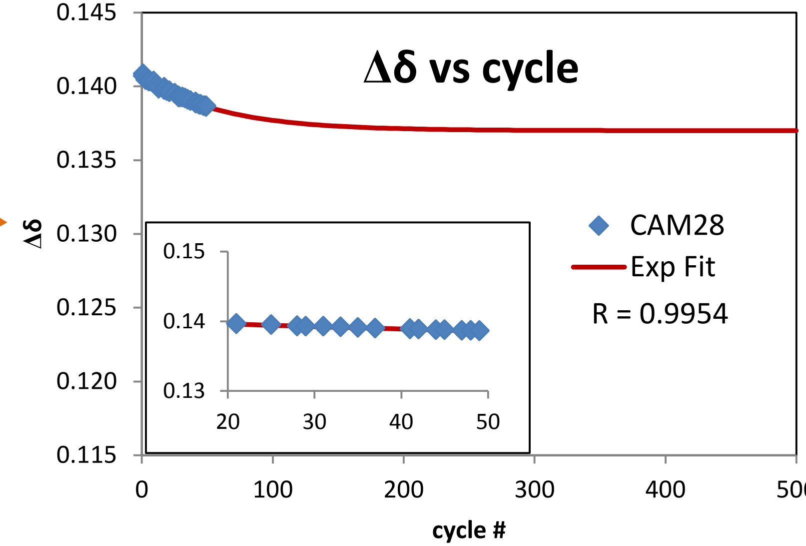


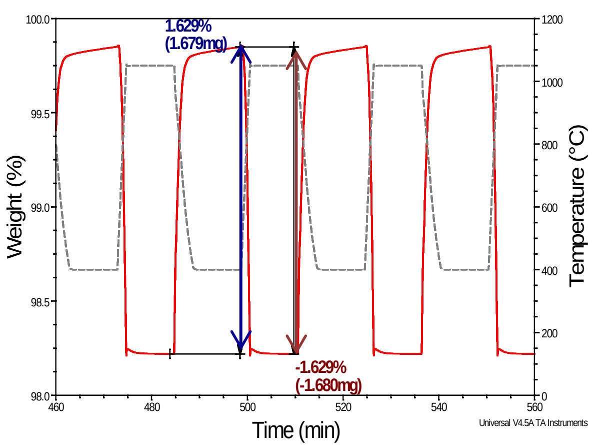
HT XRD results for: **Cam28 low_pO2**

CAM28 Cyclic Behavior

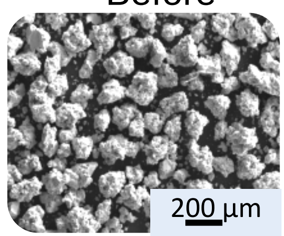
Extended thermal redox cycling in TGA



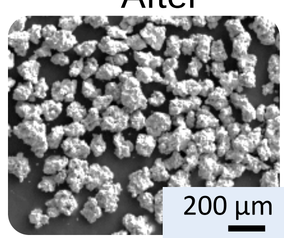




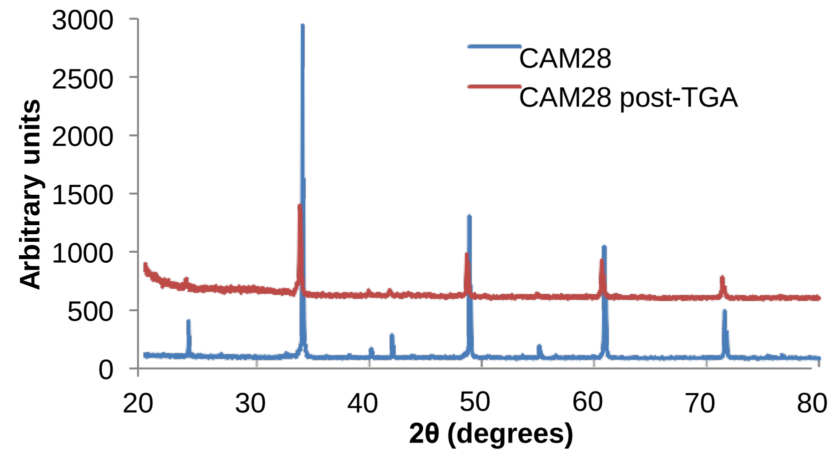
Before



After



SEM of cycled particles



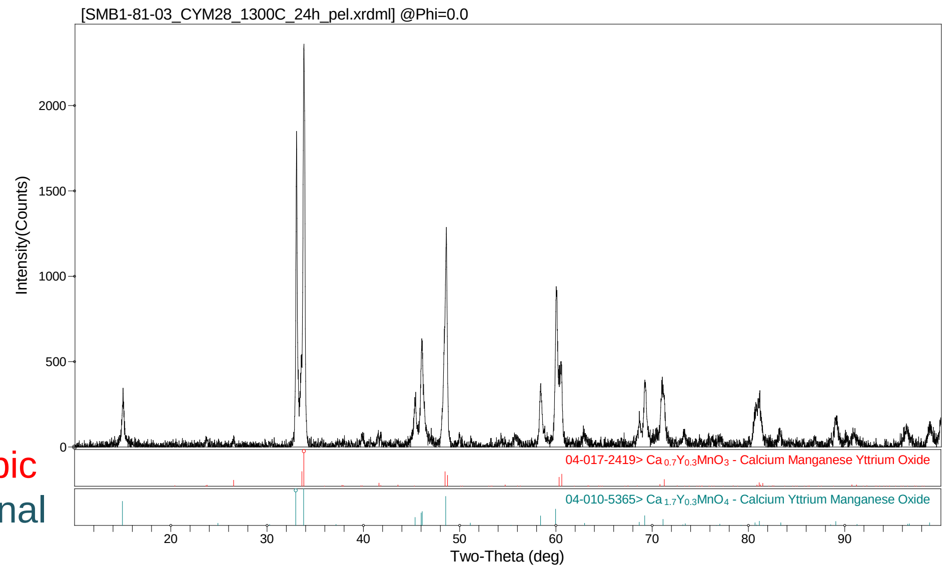
SunShot U.S. Department of Energy

Sandia National Laboratories

A-Site Doping in $CaMnO_3$

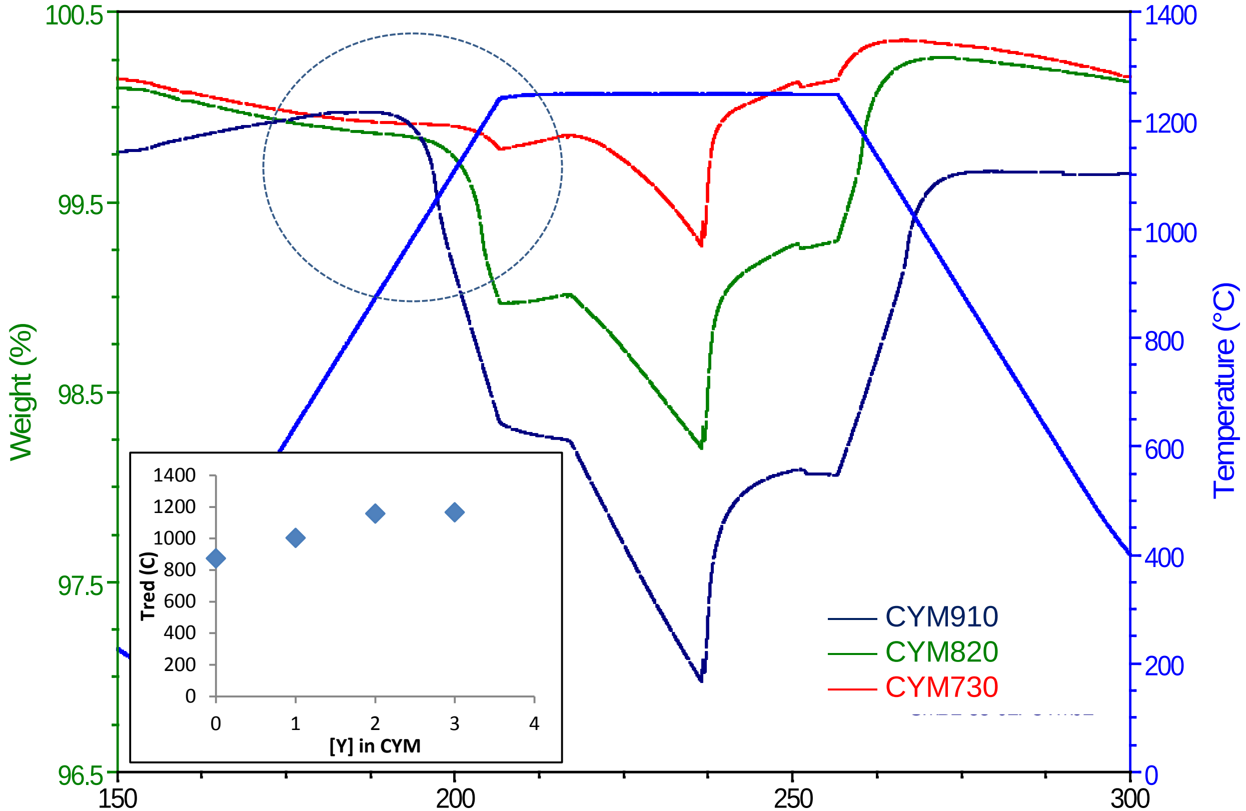
CYM28

- Analogue of CAM28
- Large increase of T_{red} - 1022 °C in air
- Not single phase
- Poor redox capacity
- Y seems to substitute on the A-site (for Ca) rather than on the B-site
    - o Increase in T_{red} observed in other A-site doped $CaMnO_3$ compositions
    - o *Can A-site doping result in an increased T_{red} while maintaining the higher redox properties of the parent compound?*



$Ca_{0.7}Y_{0.3}MnO_3$ orthorhombic
$Ca_{1.7}Y_{0.3}MnO_4$ tetragonal

$Ca_{1-x}Y_xMnO_3$ (0<x<0.5)

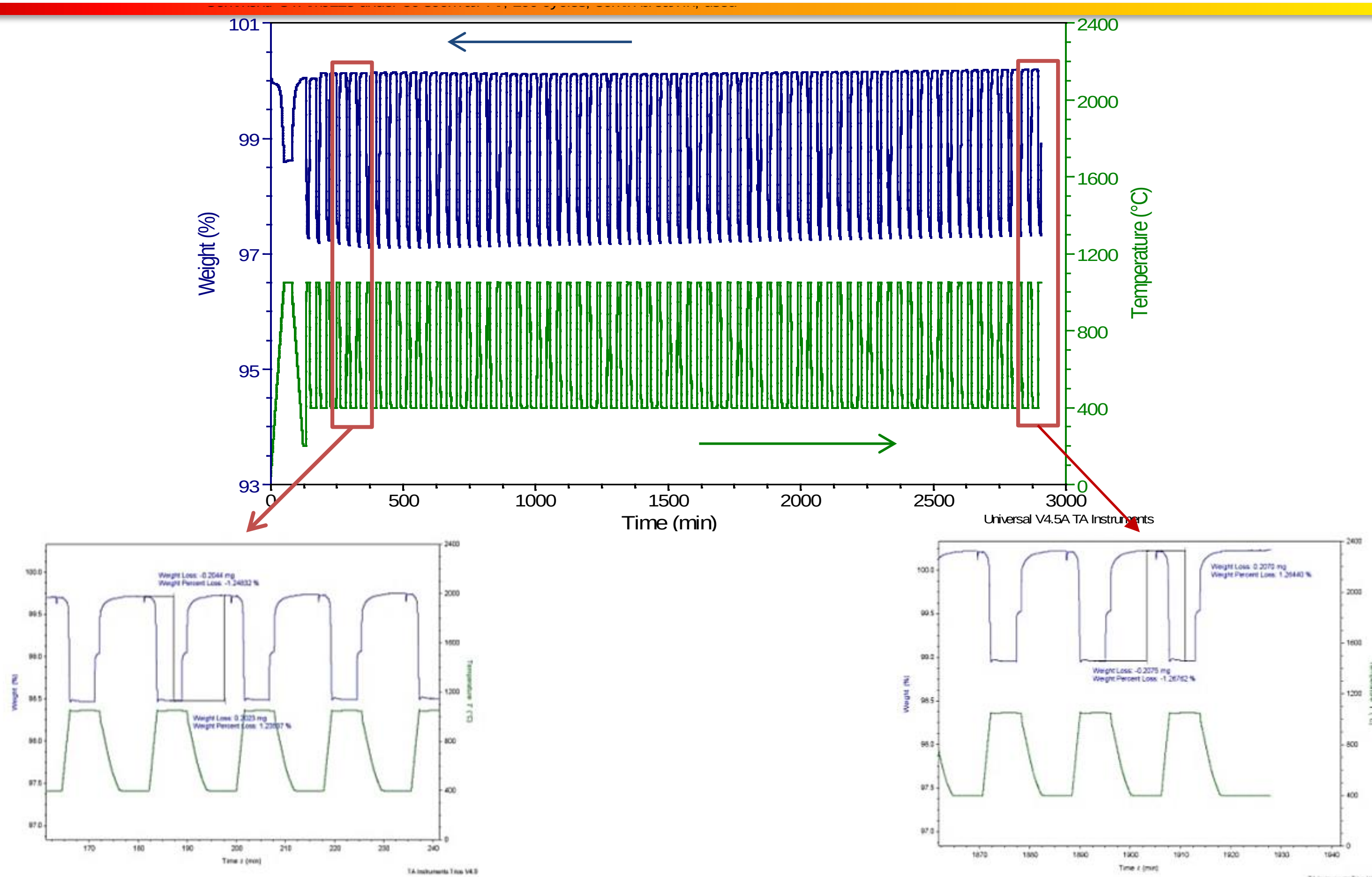


- T_{red} increases with increasing [Y]
- Corresponding δ decreases with increasing [Y]
- Balance between T_{red} and reduction extent (δ)
- At what point does T_{red} become too high?

SunShot U.S. Department of Energy

Sandia National Laboratories

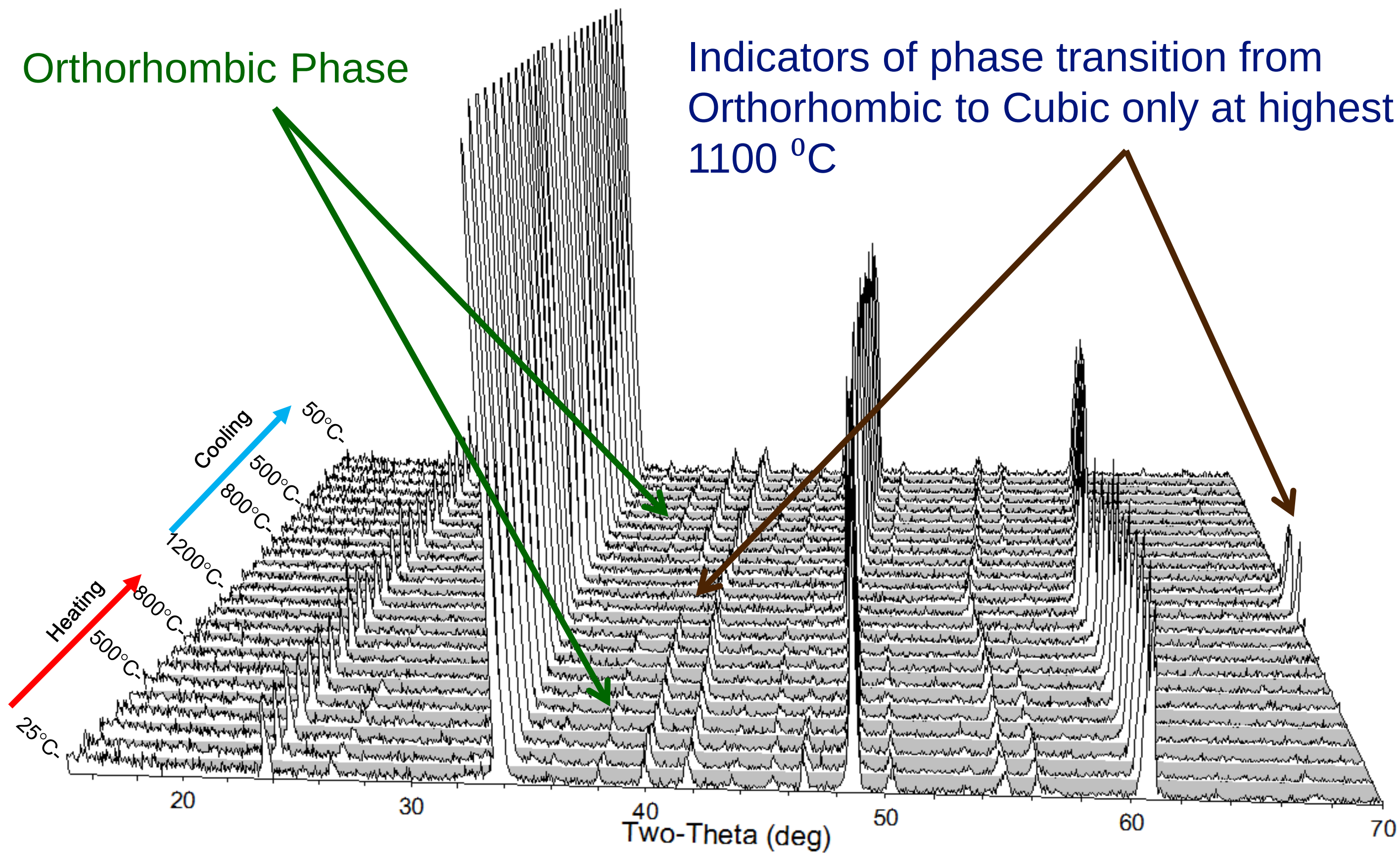
Multi-cycle TGA CYM910



- Reduction at 1050 °C/ 10% air:Ar; Oxidation at 400 °C/ air
- Reproducibility over 100 cycles
- Symmetry transition does not seem to affect kinetics
- Post-cycle XRD shows no structural change

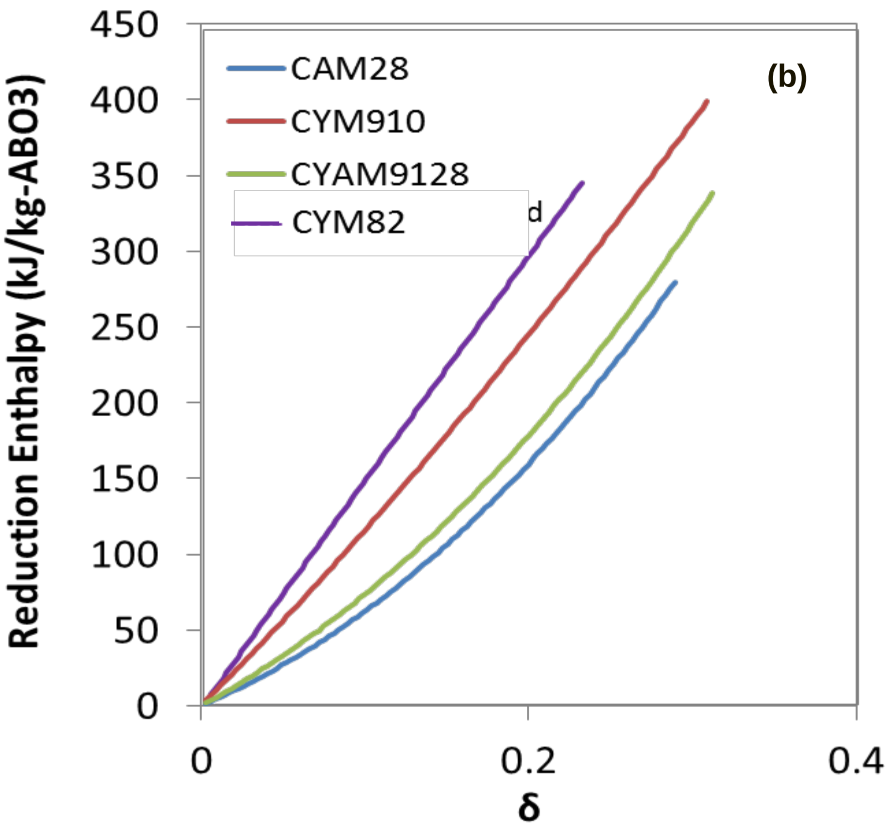
In-situ XRD CYM910

- Orthorhombic → Cubic transition also observed, but at higher temperature than CAM28
- Consistent with higher-temperature exotherm and T_{red}



In-situ X-ray diffraction of CYM910 under pO_2 = 500 ppm

Enthalpy of Y-doped $CaMnO_{3-\delta}$



- Y-doping improves enthalpy over CAM28
- CYM910 ΔH ~ 400 kJ/kg
- Potential of higher enthalpy with increasing [Y] if effective δ can be increased
- Tradeoffs between higher enthalpy and costs of [Y] must be determined

While T_{red} eventually becomes impractical, insights gleaned from these trends can aid in design of future materials with tunable enthalpies and reduction temperatures

Conclusions

- Initial LSCX investigation provided insight on structural/thermal properties of TCES perovskites
    - Promising ΔH_{total} values achieved, but reduction extent is adequate, but reaction enthalpy falls short of 1500 kJ/kg goal
- Reduction onset temperature (T_{red}) was identified as a key indicator of ΔH_{rxn}
- $CaMnO_3$ displays high T_{red} but decomposes under reducing conditions
- B-site doping with non-labile cations (Al, Ti) mitigates decomposition while maintaining redox properties
    - ΔH_{total} approaching1500 kJ/kg
    - Increase in reaction enthalpy of over 50% compared to LSXM
    - *To our knowledge these materials outperform any reported oxide TCES material operating above 1000 °C*
- A-site doping with Y further increases T_{red}
    - Sacrifice redox extent
    - What is the ideal balance between T_{red} and δ?
- Judicious choice of A- and B- sited dopants in $CaMnO_3$ can result in effective TCES materials across a wide range of operating parameters

Acknowledgements

- The PROMOTES Team (Georgia Tech, King Saud University, Arizona State University)
- Peter Loutzenhiser (Georgia Institute of Technology)
- Ellen Stechel (Arizona State)
- Shannon McKean (USNA)
- Bonnie McKenzie (Sandia)
- Mark Rodriguez (Sandia)
- Travis Anderson (Sandia)
- National Solar Thermal Test Facility at Sandia National Labs

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525

Grazie

Thank You

Danke

ευχαριστώ

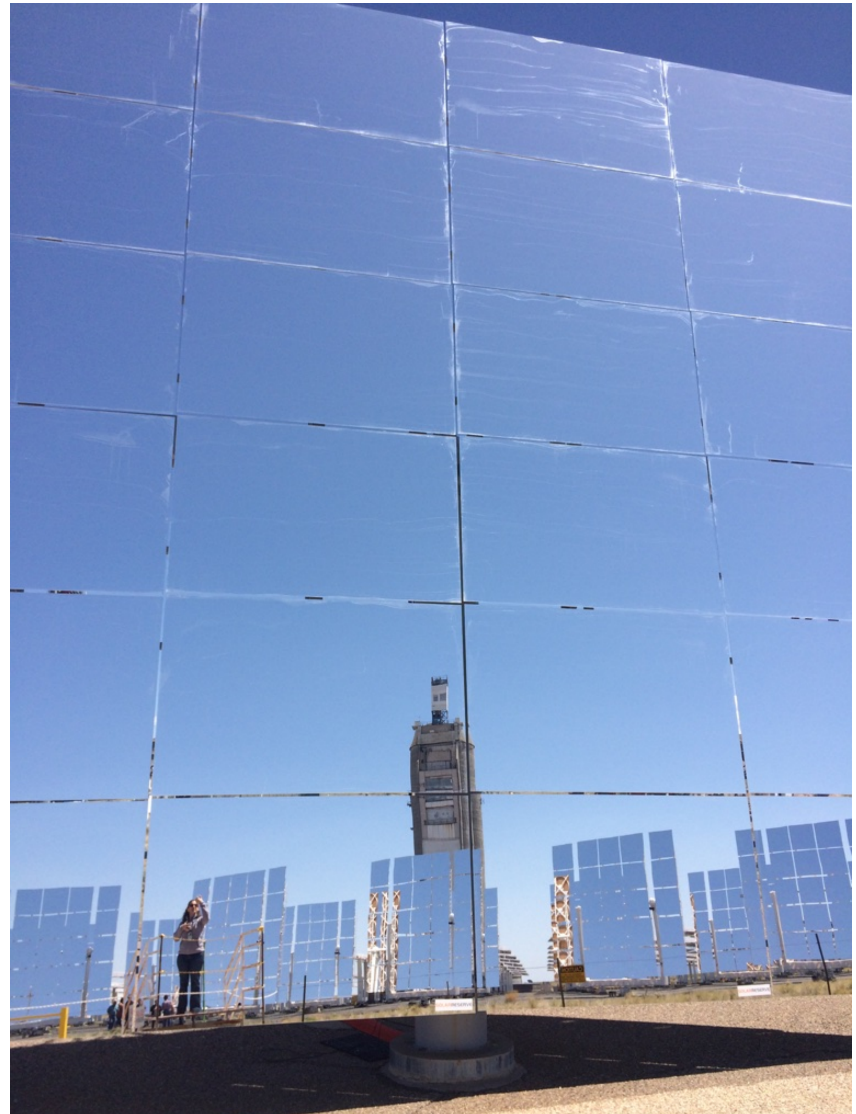
Gracias

ти благодарам

Merci

Спасибо

ありがとうございました



SunShot U.S. Department of Energy

Sandia National Laboratories