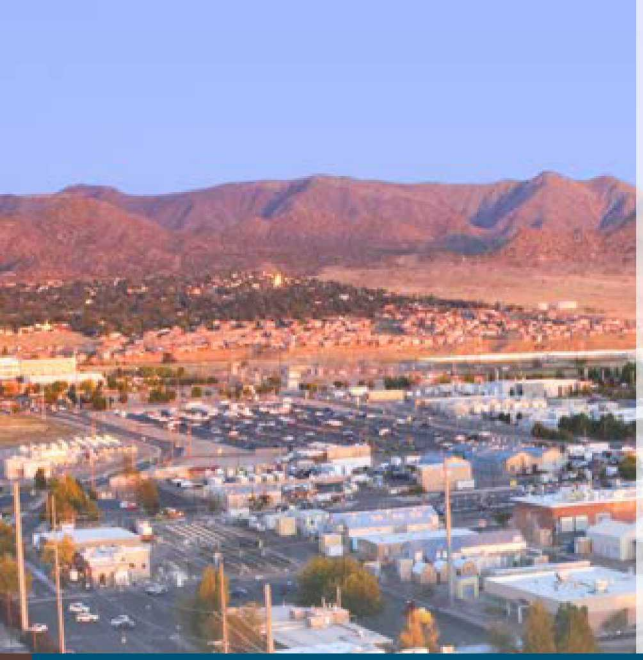

SAND2019-9476PE

# Thermochemical Energy Storage Using Redox-Active Metal Oxides

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DRESDEN Workshop

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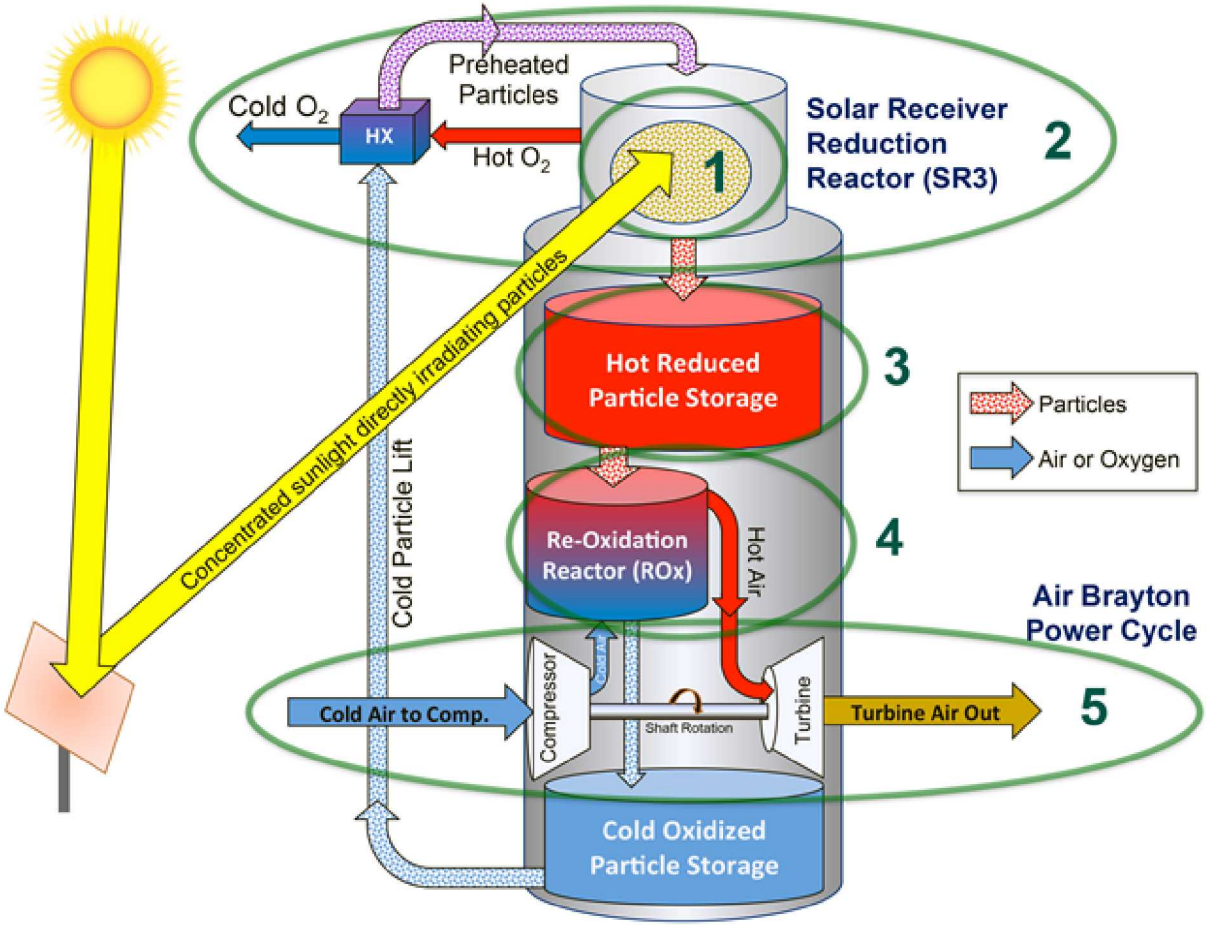
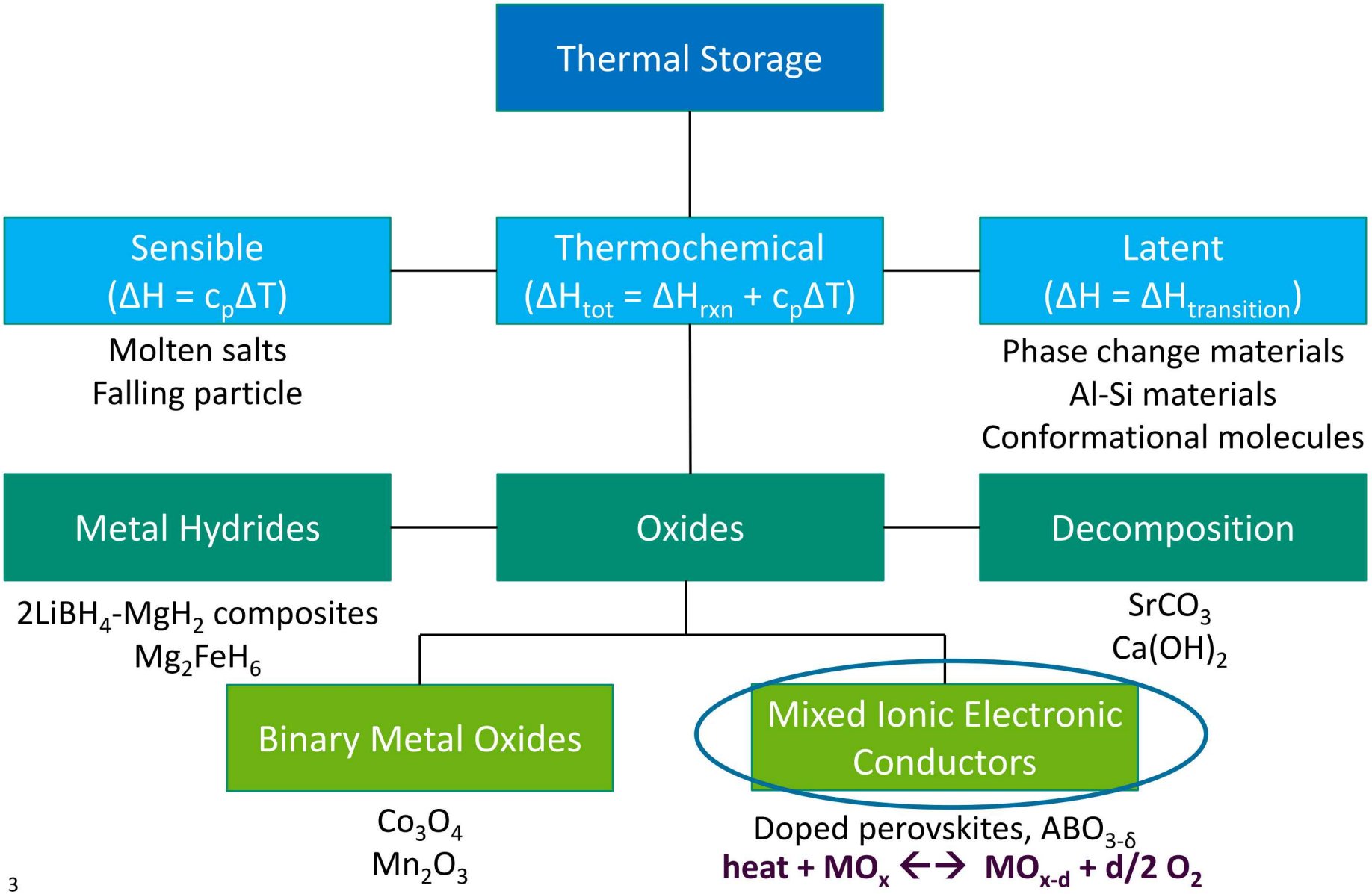
# PROMOTES

## High Performance Reduction/Oxidation Metal Oxides for Thermochemical Energy Storage



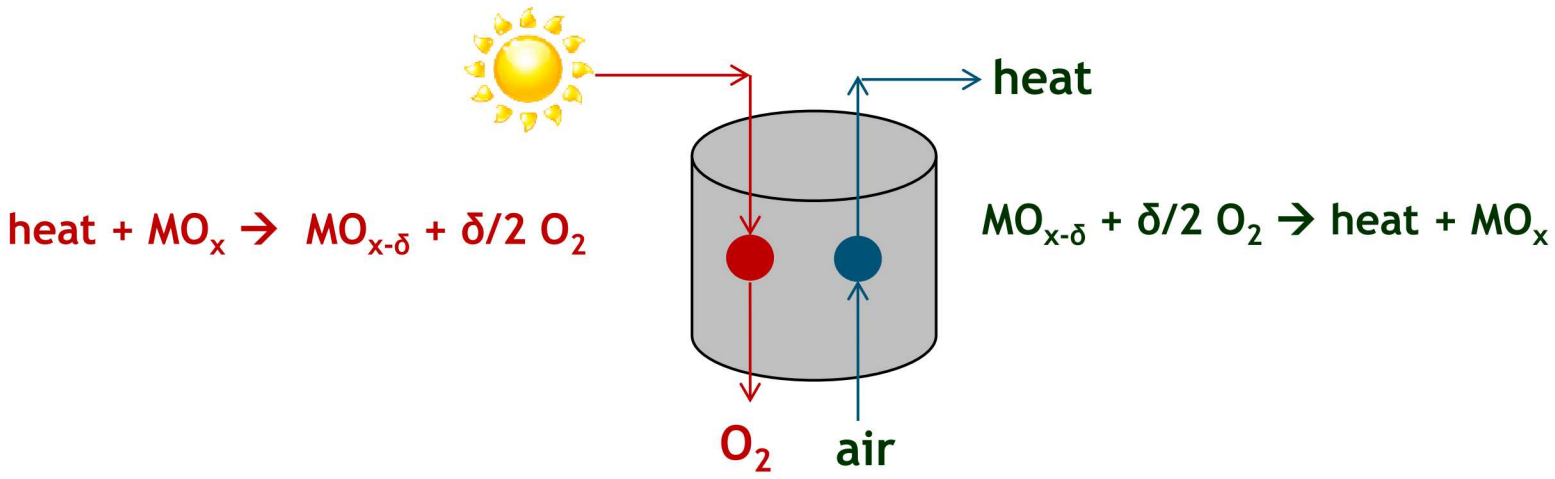

1. Materials Enabled Innovation ($\Delta H_{total} \geq 1500$ kJ/kg)
2. Solar Receiver Reduction Reactor
3. Particle Storage at T > 1000 ºC
4. Pressurized oxidation reactor Air acts as reactant and heat transfer fluid. Open cycle – no gas storage.
5. High Temp/High Efficiency Air Brayton Power Cycle.

# Thermal Storage in CSP



# Metal Oxide TCES

Metal oxides are ideal materials for storage in high temperature cycles




- 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

# Complex Oxides

**Metal Oxides**

- Leverage both sensible heat and heat of reaction
- High energy density, extended temperature range, compatible with high efficiency power cycles
- State-of-the-art is binary oxides - limited kinetics & tunability, questionable longevity, redox activity tied to phase change

**Mixed Ionic-Electronic Conductors**

- Exhibit both electronic and ionic conductivity
- Ionic conductivity facilitates oxygen transport--improved kinetics and reaction extent
- Electronic conductivity facilitates redox activity

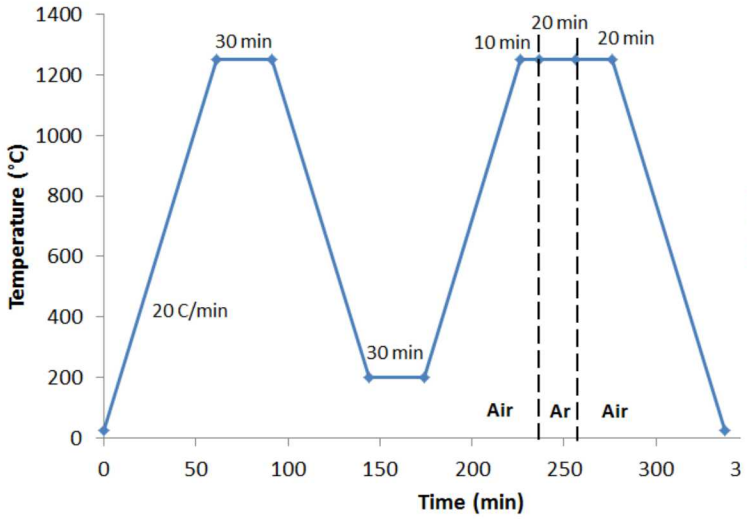
**Perovskite Oxides**

- General formula $ABO_{3-\delta}$ ($\delta$ = oxygen nonstoichiometry)
- Amenable to doping --tunability of redox extent and temperature
- Oxygen nonstoichiometry enables redox activity without structure decomposition

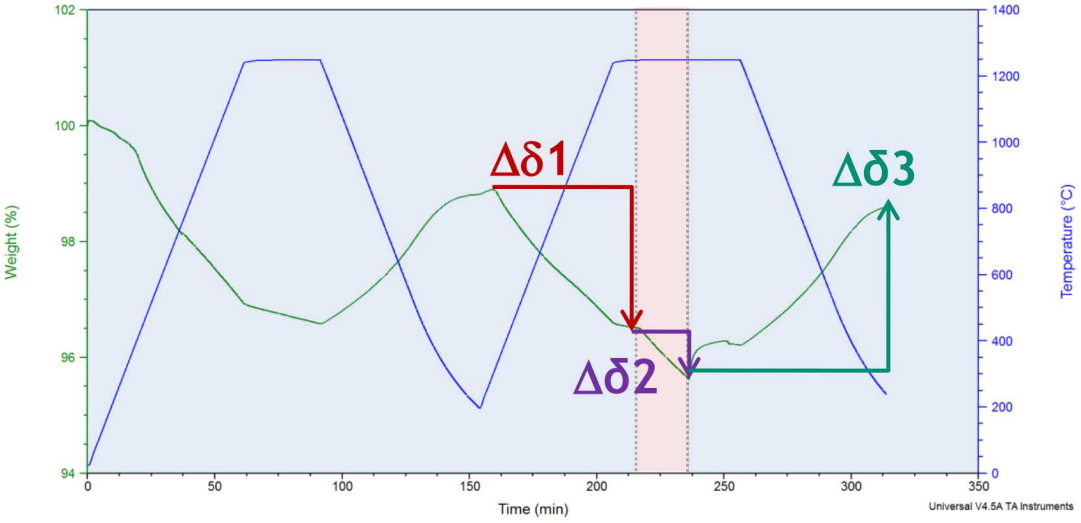
# Materials Screening Effort

- Build upon known redox-active perovskites, e.g., doped $La_xSr_{1-x}MnO_{3-\delta}$ ("LSM")
- Tune properties via A- and B-site cation substitution
  - A = K, Ba, La Sr; B = Fe, Co, Mn
- X-ray diffraction (XRD) to determine crystal structure and identify impurities
- Initial non-equilibrium thermogravimetric analysis (TGA) used to determine potential redox activity and reduction onset temperature

Mass change measured as a function of temperature and $pO_2$




Pre-screen method

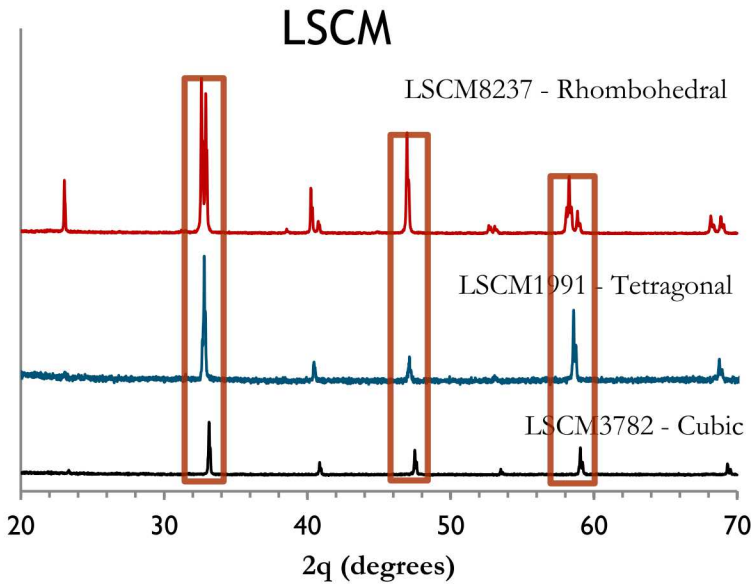


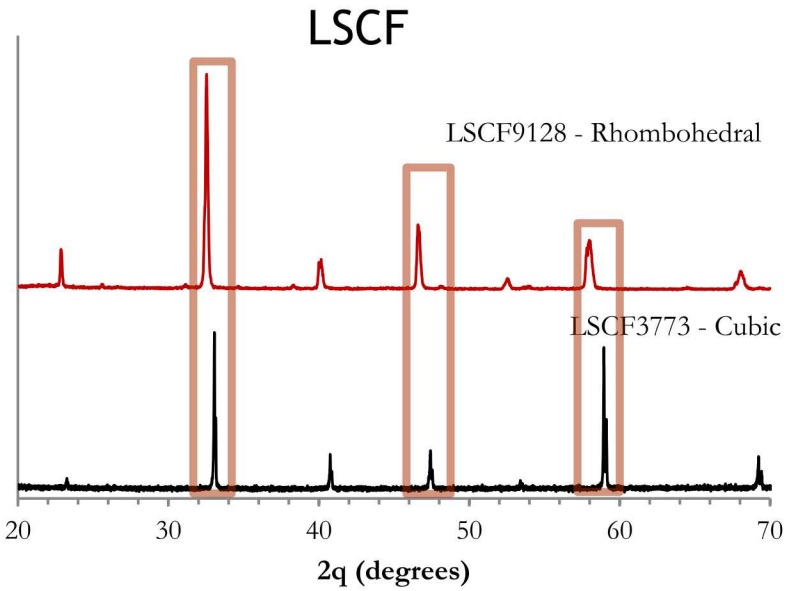

Example TGA

# Doped LaCoO3

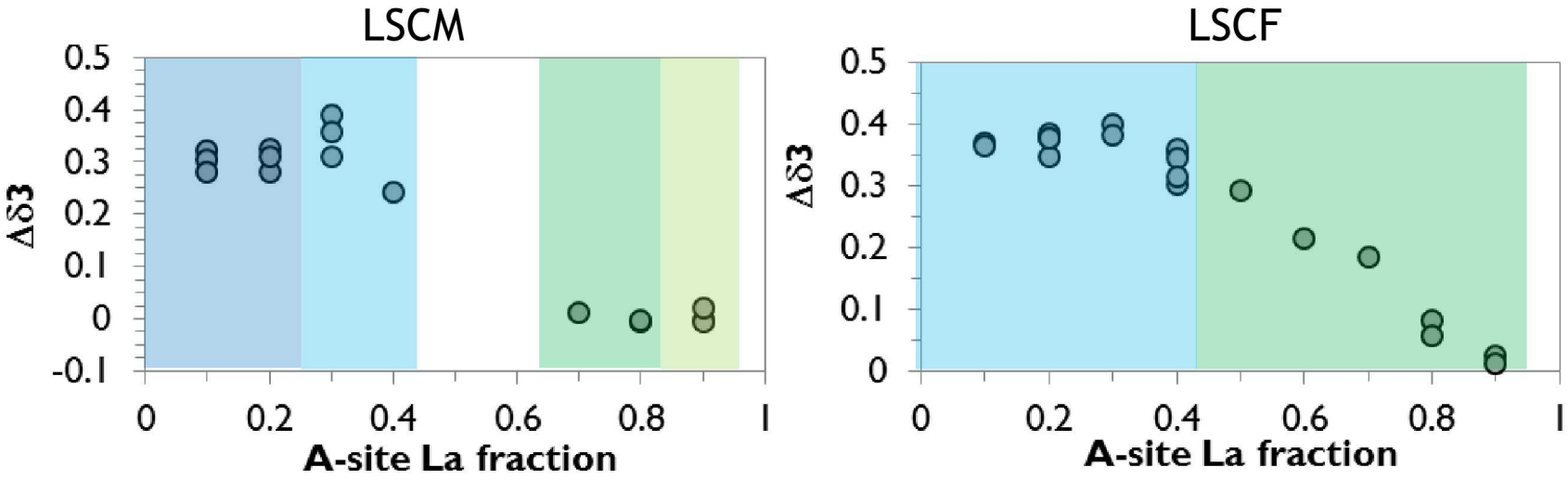
## $La_xSr_{1-x}Co_yMn_{1-y}O_{3-\delta}$ (LSCM) and $La_xSr_{1-x}Co_yFe_{1-y}$ (LSCF)

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



# A-site (La) Substitution

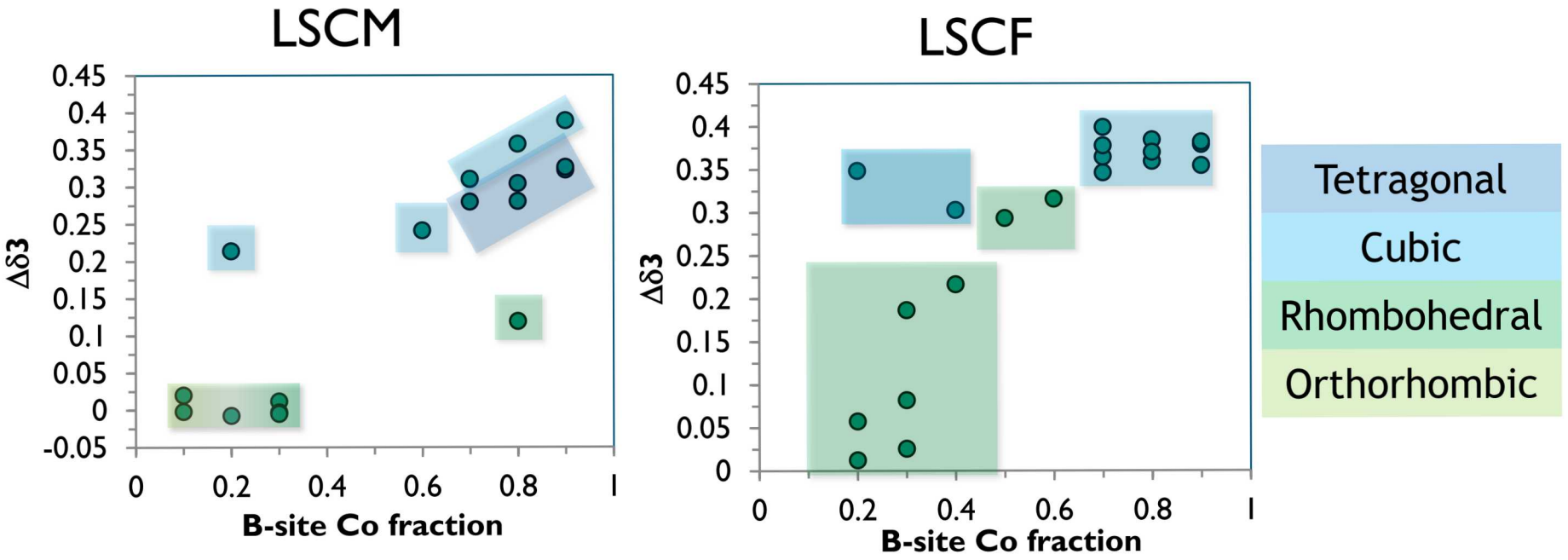



| |
|---|
| Tetragonal |
| Cubic |
| Rhombohedral |
| Orthorhombic |

- Tetragonal and cubic structures are most redox active
- Lower [La] results in more symmetric space groups.
- High [La] produces less symmetric space groups.
- Redox activity decreases with increasing lattice distortion
- In both families redox seems to peak at [La] = 0.3 (cubic)

# B-site (Co) Substitution

- Cobalt content has a weak correlation to redox activity
  - Increased cobalt content generally increases Δd
  - Crystal structure is not a strong function of Co content

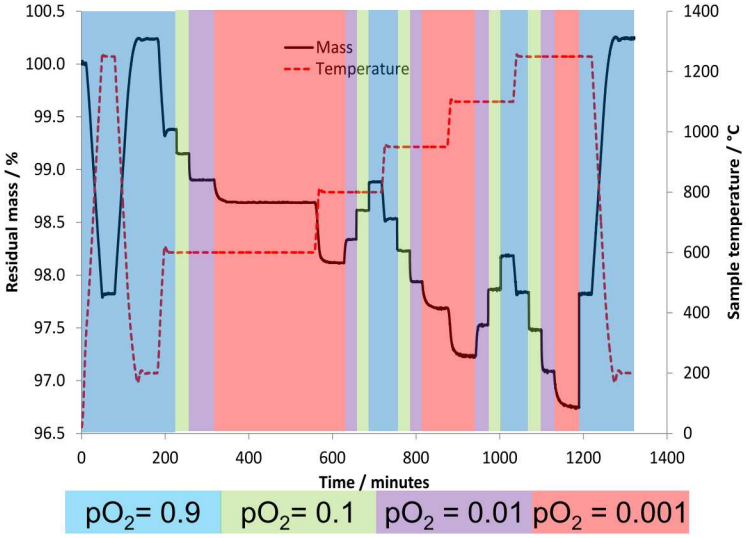


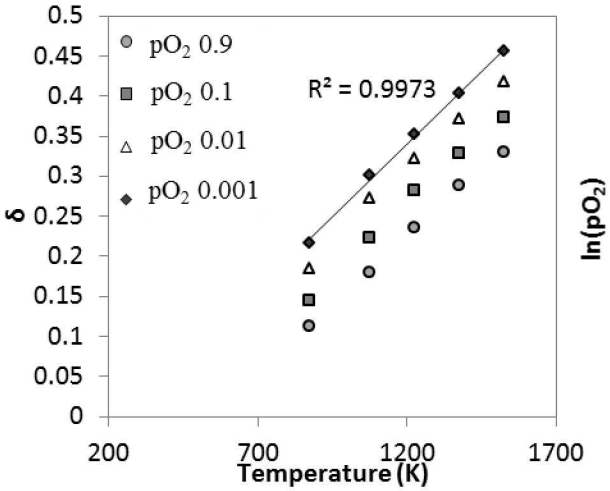
# High-Resolution Equilibrium TGA

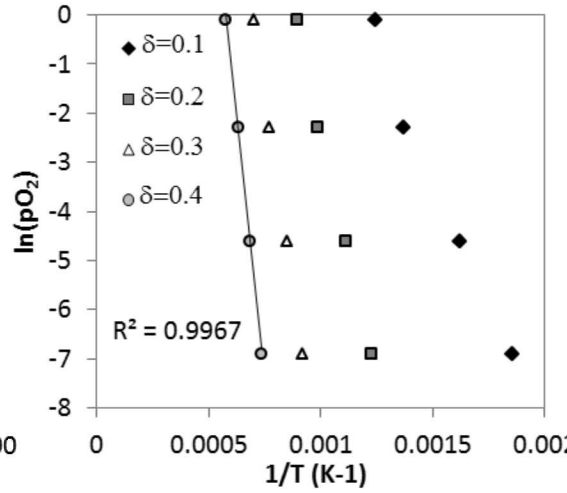
- Used to estimate thermodynamic parameters
- Isothermal holds at 600, 800, 950, 1100, and 1250 ºC; pO2 varied at each temperature and held until equilibrium
- Thermodynamic parameters extracted by van't Hoff approach:

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

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

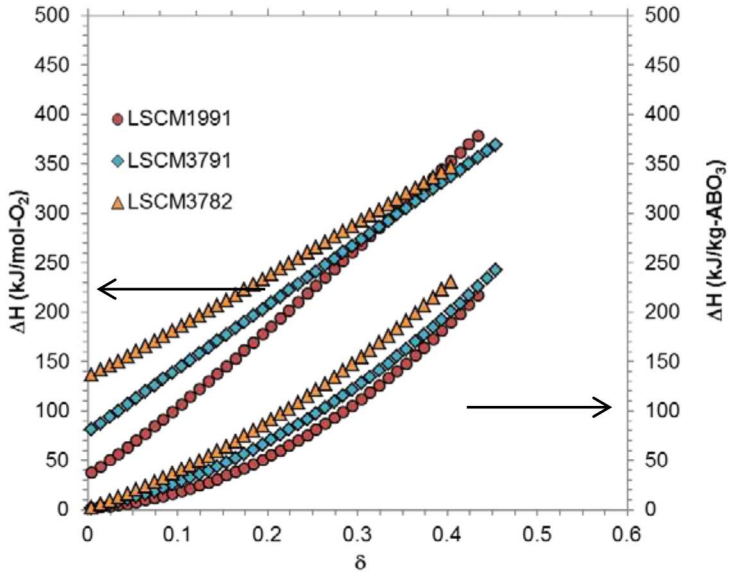


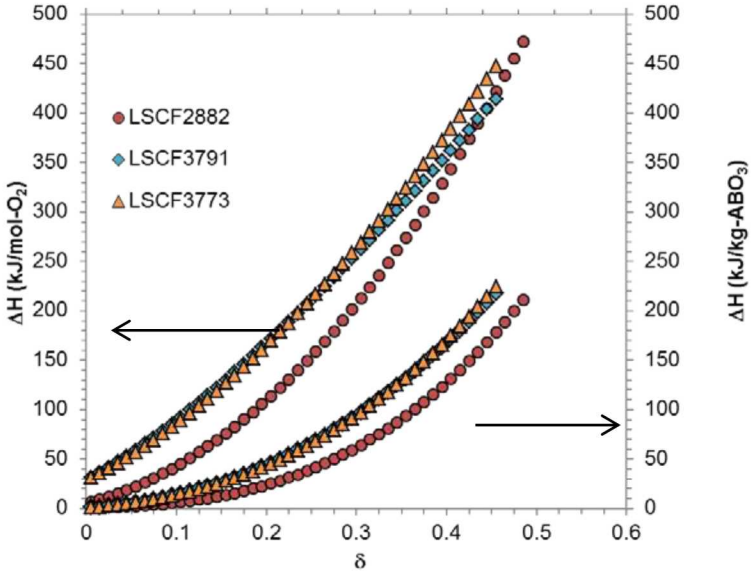



# LSXM Enthalpy

- 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

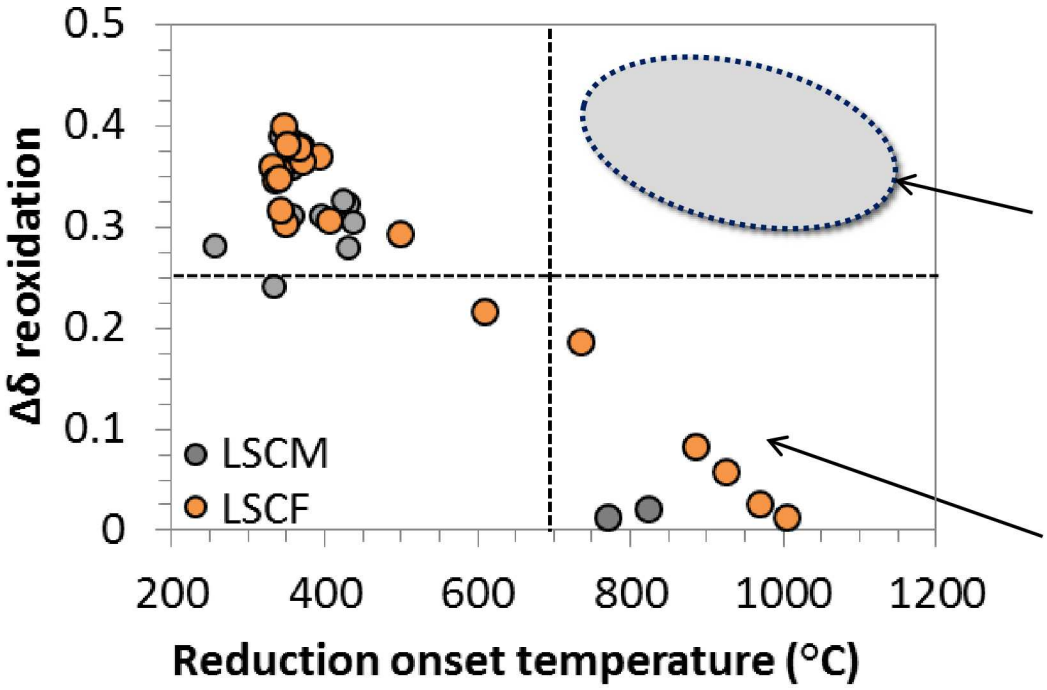



| Material | Reduction onset (°C) | Maximum δ | Enthalpy at $\delta_{max}$ (kJ/kg) |
|---|---|---|---|
| **LSCM1991** | 432 | 0.434 | 216 |
| **LSCM3791** | 343 | 0.460 | 242 |
| **LSCM3782** | 359 | 0.412 | 236 |
| **LSCF2882** | 357 | 0.486 | 212 |
| **LSCF3791** | 352 | 0.461 | 223 |
| **LSCF3773** | 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.

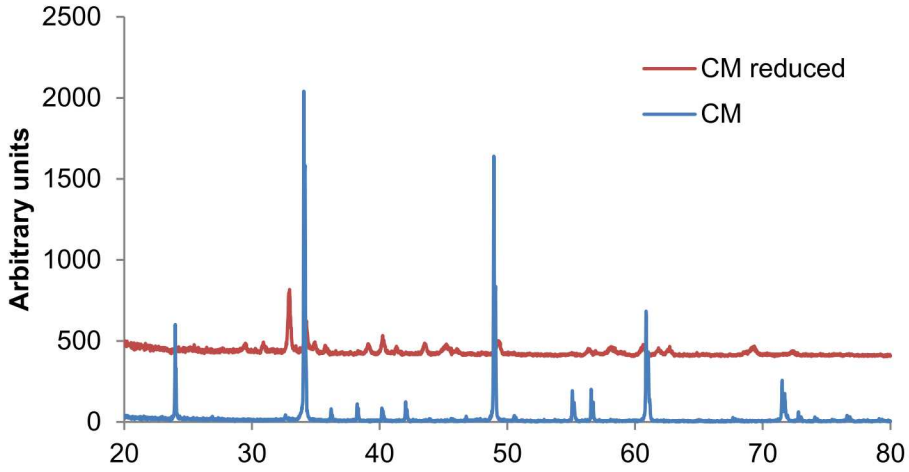
In the LSCX system, materials with high reduction temperatures had low redox capacity ($\delta < 0.25$).

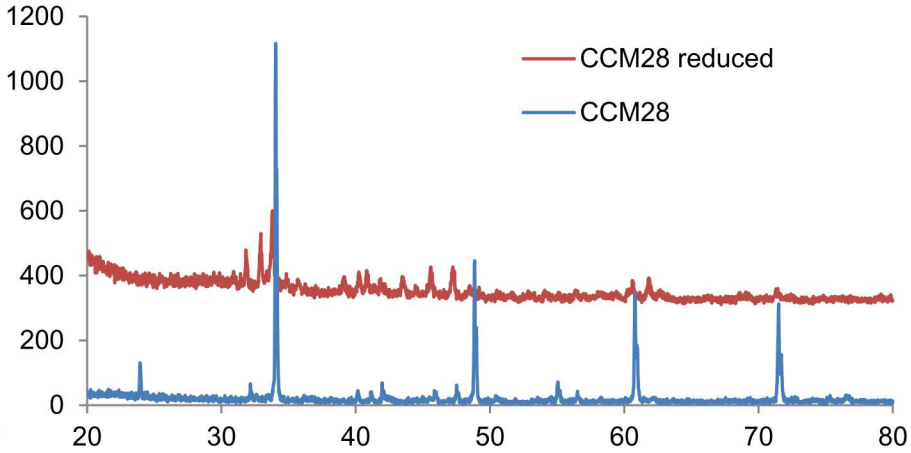
# Doped $CaMn_{1-y}B_yO_{3-\delta}$ Perovskites

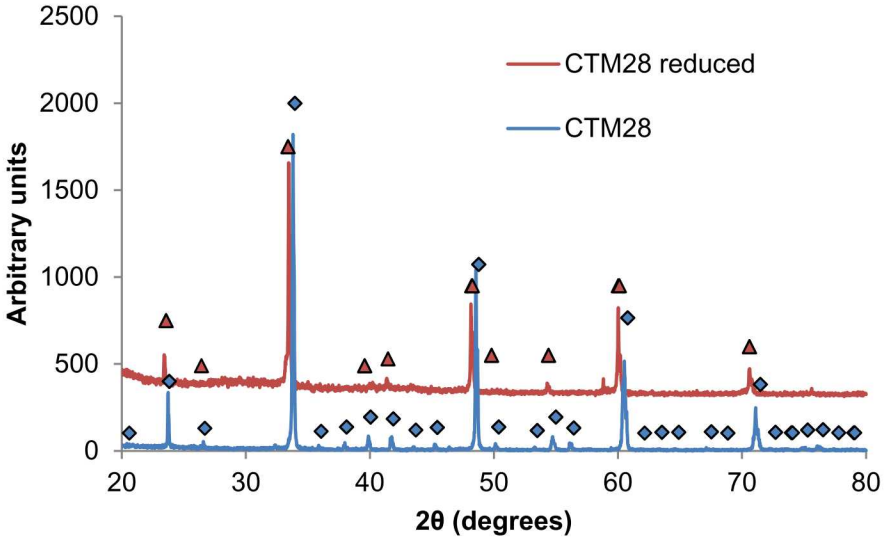
- Ca is a +2 element, forcing the B-site, e.g. Mn, to adopt a higher oxidation state (+4)
- Ca as the main element in the A-site lowers the molecular weight dramatically (Ca = 40.078 g/mol)
- Ca more abundant and less expensive than Sr or La
- Calcium-based perovskites reduce at high temperatures,
  - Higher reduction temperatures indicative of stronger M-O bonds, resulting in increased partial molar reduction enthalpies
- $T_{red}$ of CaMnO3 = 875 °C (vs. 432 °C for LSCM1991)
  - However, decomposes under reducing conditions
  - Doping CMO can help stabilize the structure

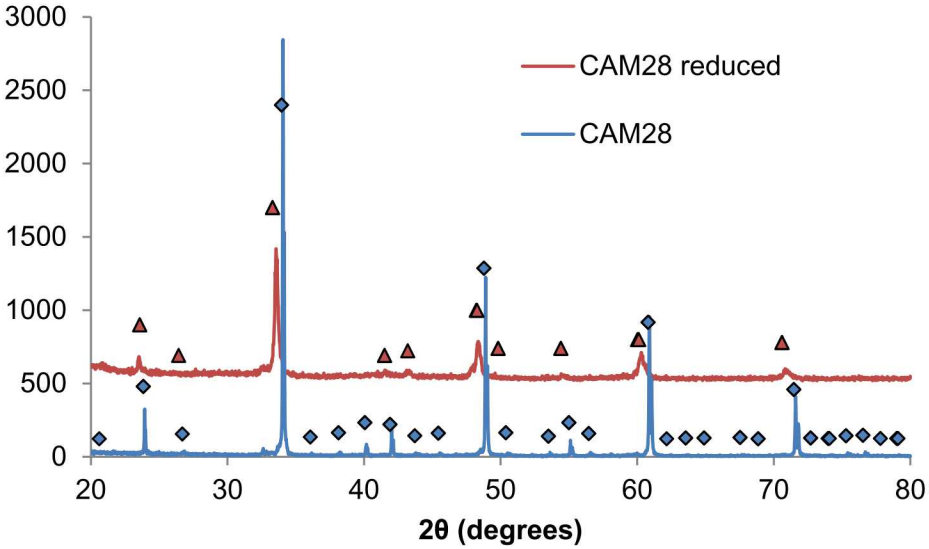
# Stability Under Reducing Conditions

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



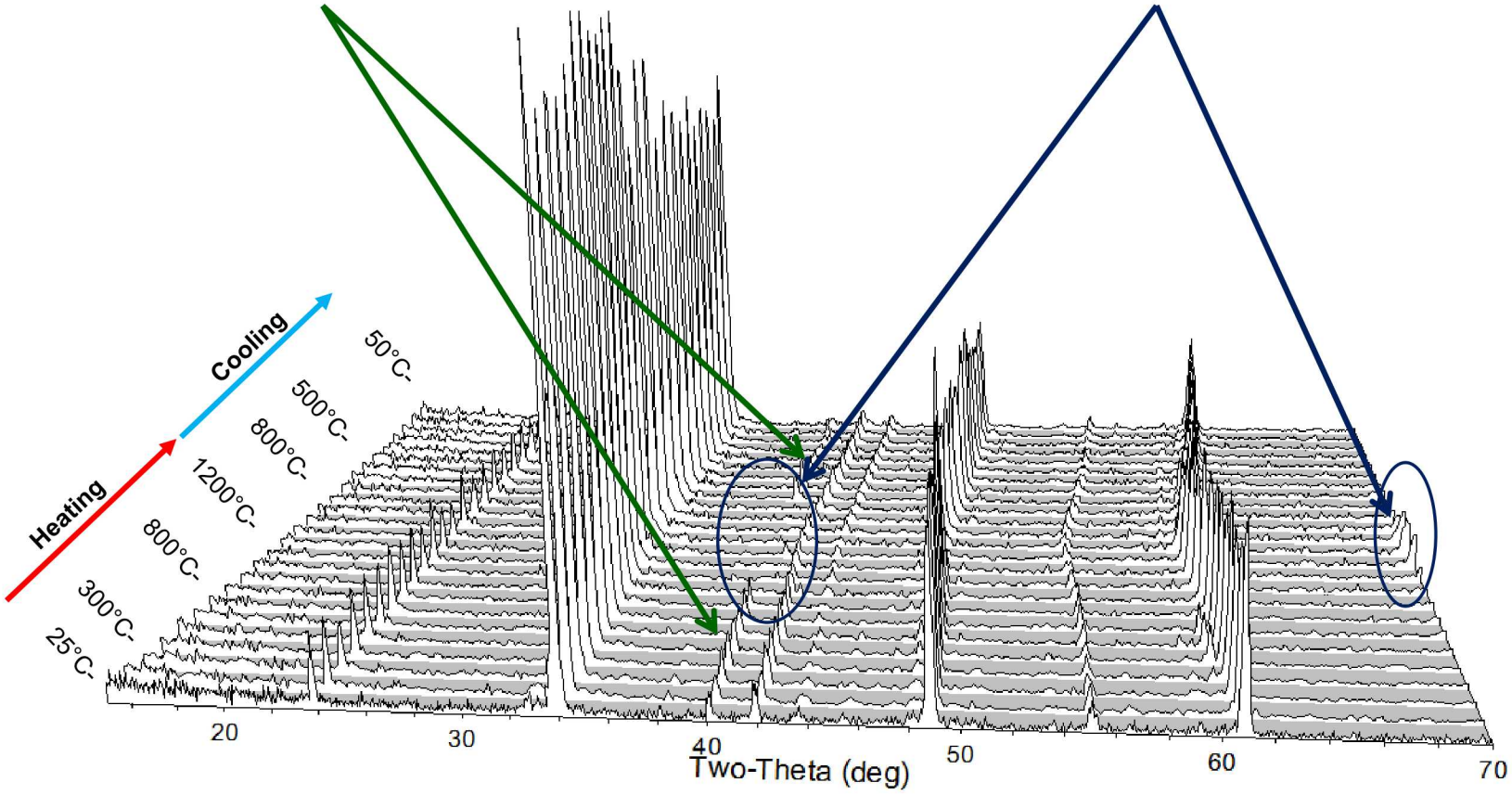



# CAM28 In-situ XRD

Orthorhombic Phase

Indicators of phase transition from Orthorhombic to Cubic-like phase at High Temperature (1000 $^{o}$C to 1200 $^{o}$C )




HT XRD results for: CAM28 low_pO2

# 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 ºC

LSCM379

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

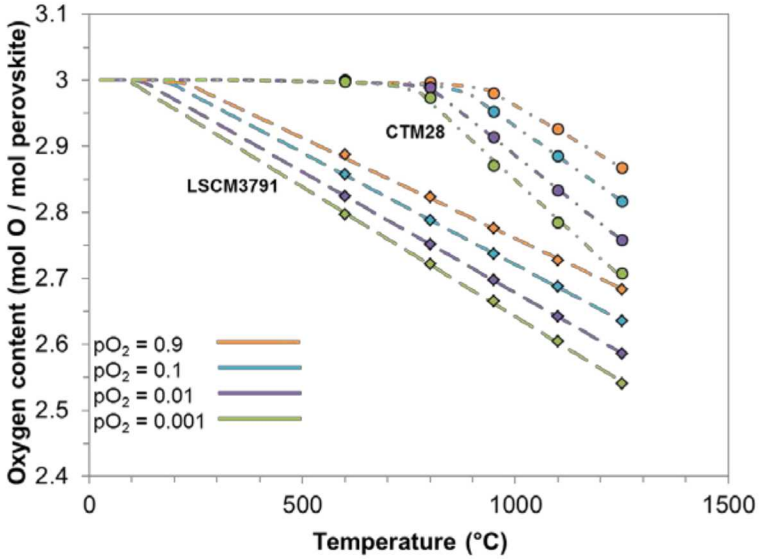
CTM2

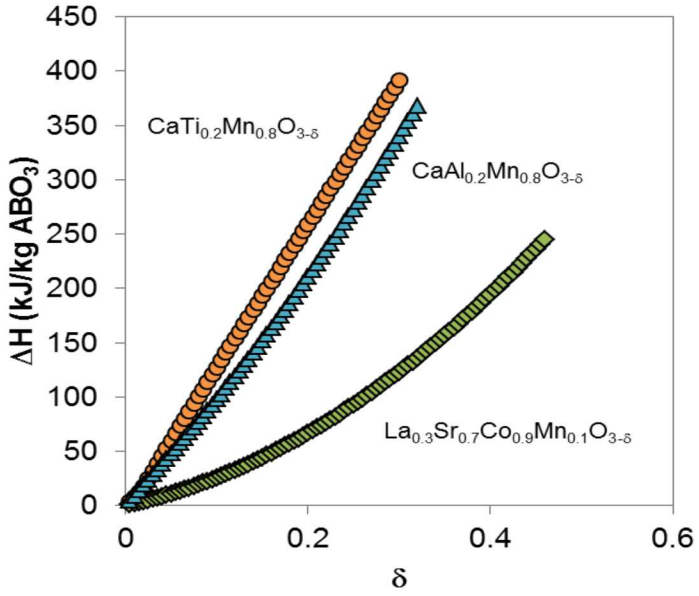
| Temperature (˚C) | Sensible (kJ/kg) | Latent (kJ/kg) | Total (kJ/kg) |
|---|---|---|---|
| 1100 | 793 | 290 | 1083 |
| 1200 | 881 | 362 | 1243 |
| 1350* | 1013 | 481* | 1494 |

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 ºC are extrapolated from δ vs T data

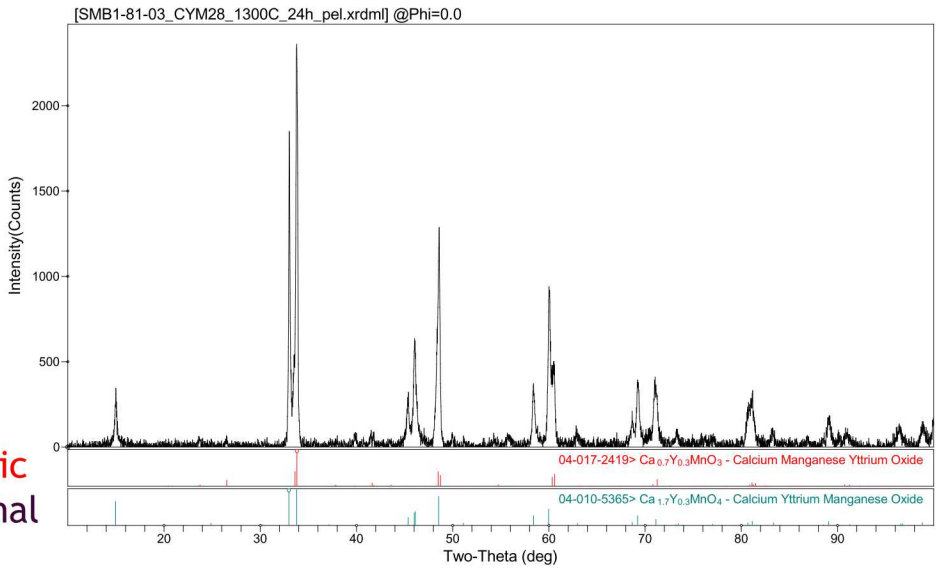


# A-Site Doping in CaMnO3

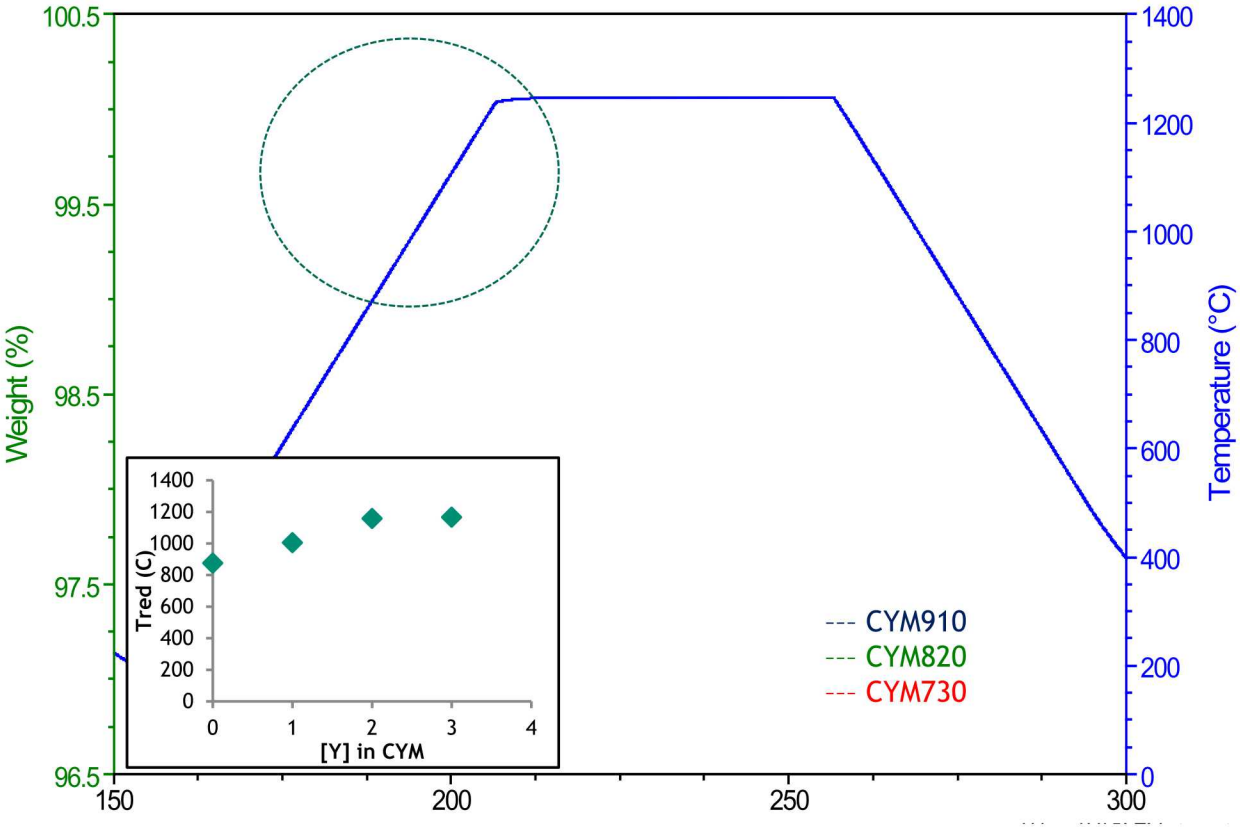
## CYM28

- 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
  - Increase in Tred observed in other A-site doped $CaMnO_3$ compositions
  - 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

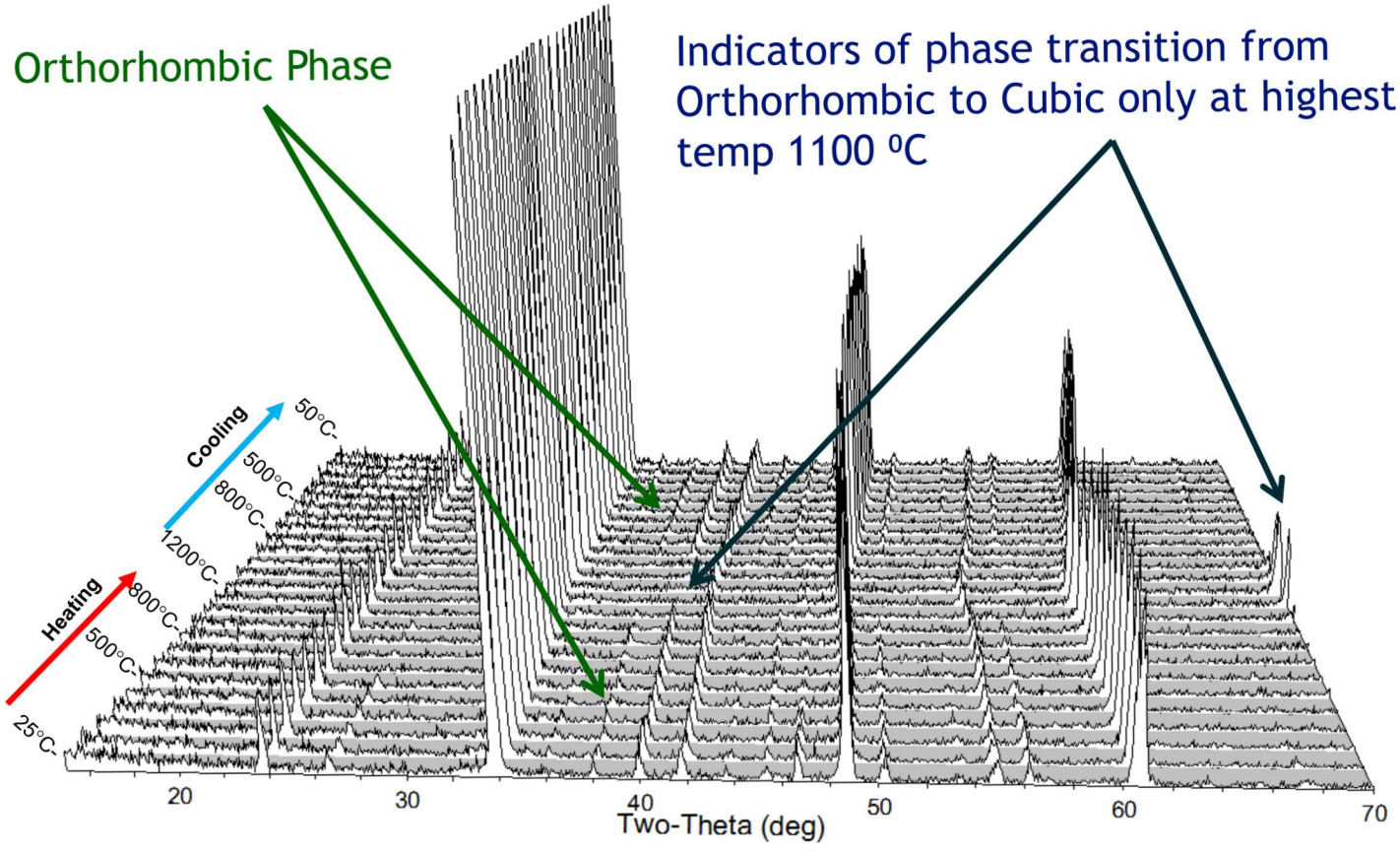
# $Ca_{1-x}Y_xMnO_3$ (0<x<0.5)




- $T_{red}$ 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?

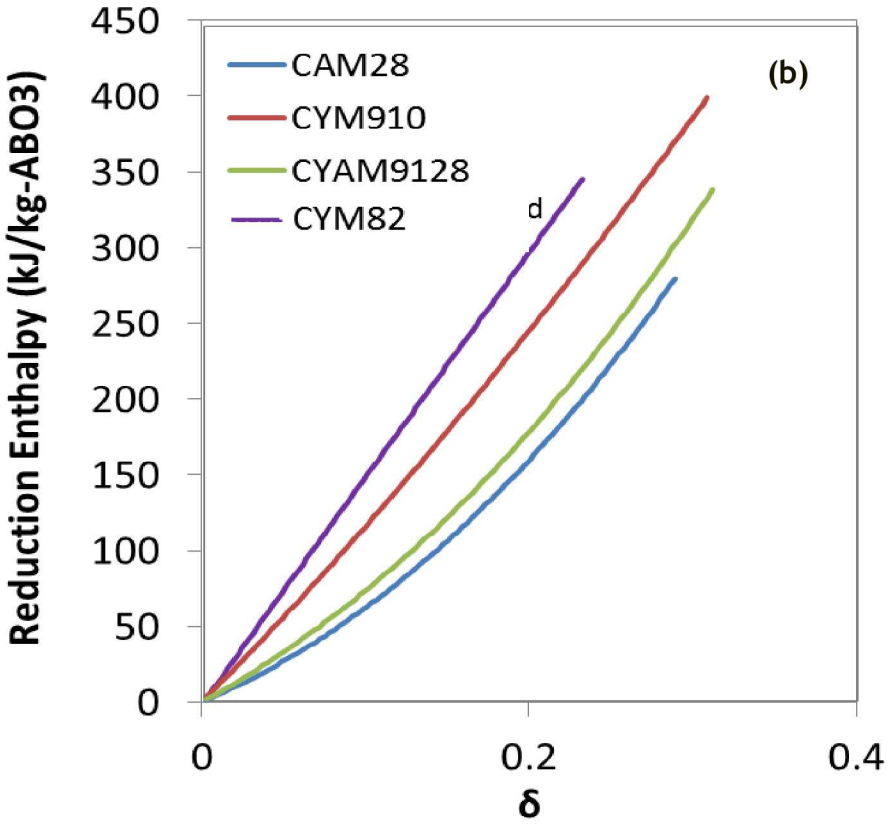
# In-situ XRD CYM910

- Orthorhombic → Cubic-like 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 ΔHtotal values achieved, but reduction extent is adequate, but reaction enthalpy falls short of 1500 kJ/kg goal
- Reduction onset temperature (Tred) was identified as a key indicator of $\Delta H_{rxn}$
- $CaMnO_3$ displays high Tred but decomposes under reducing conditions
- B-site doping with non-labile cations (Al, Ti) mitigates decomposition while maintaining redox properties
  - ΔHtotal 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)
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- Mark Rodriguez (Sandia)
- Travis Anderson (Sandia)
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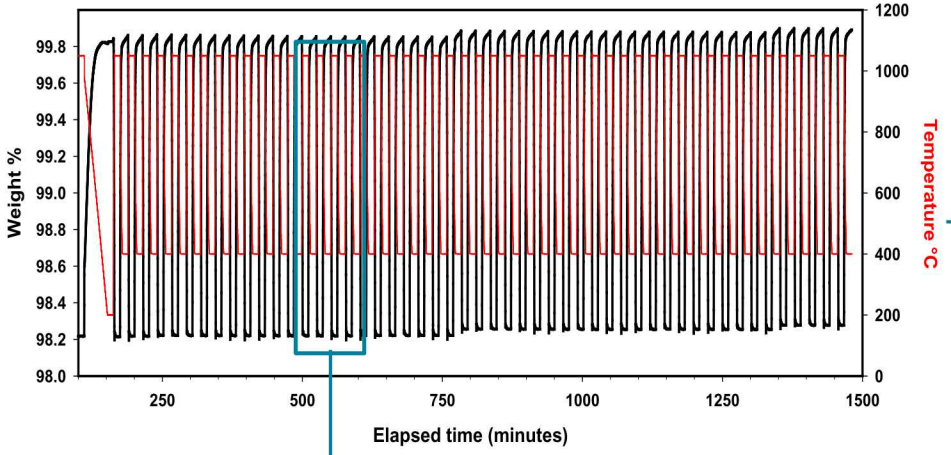
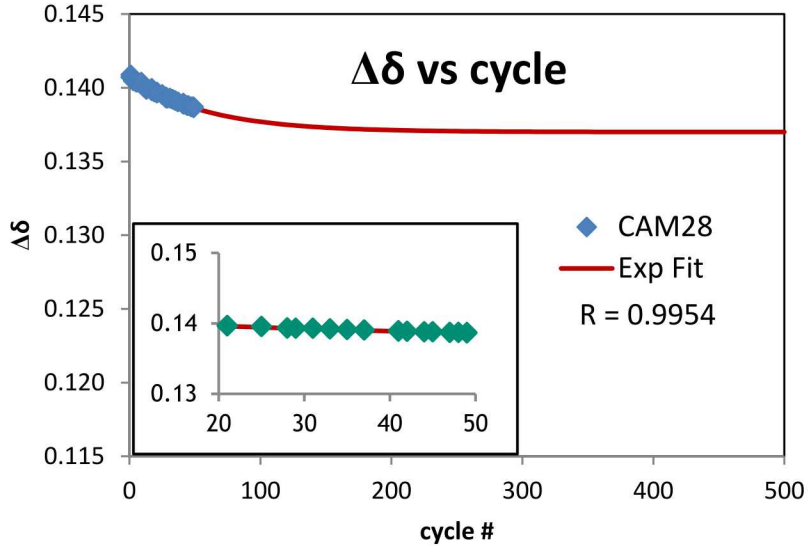
# Thank You

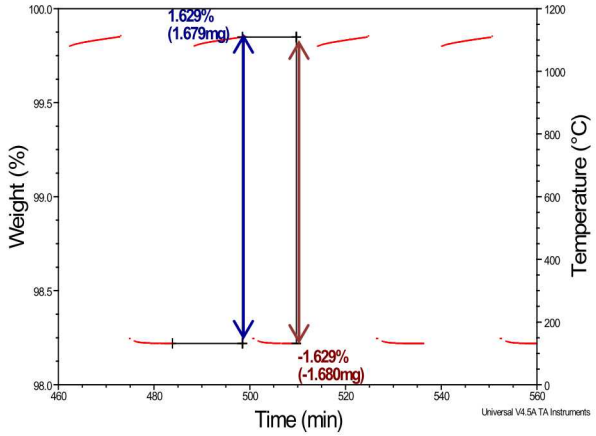
# Danke

# CAM28 Cyclic Behavior

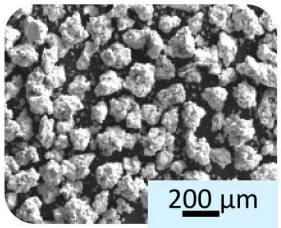
## Extended thermal redox cycling in TGA



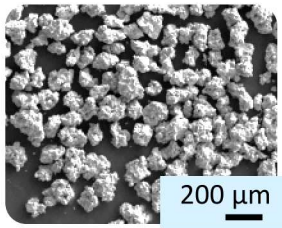



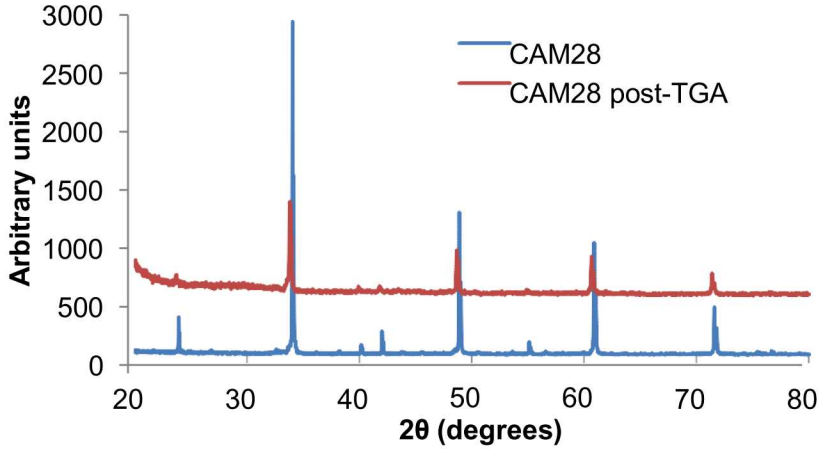




Before



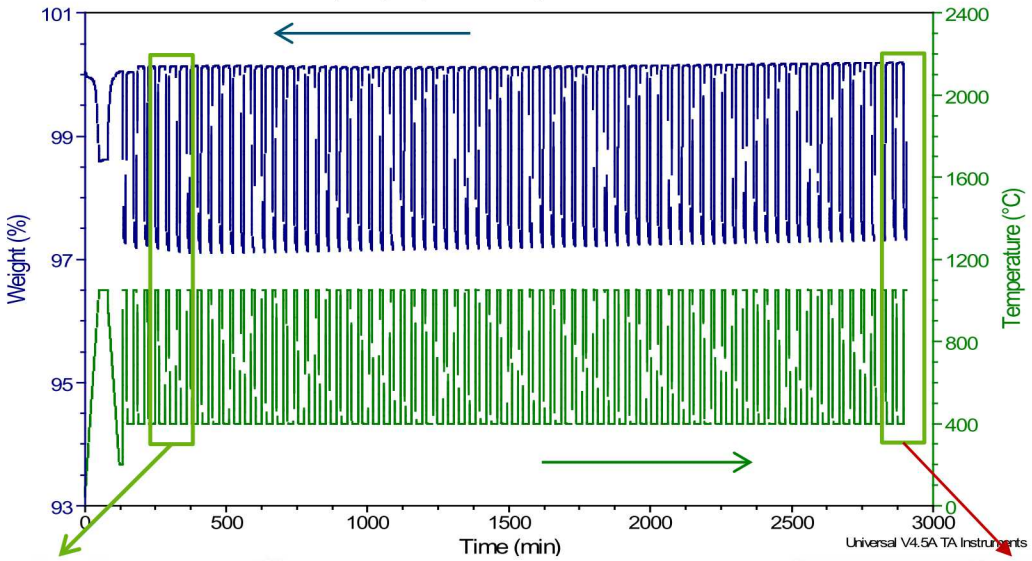

After

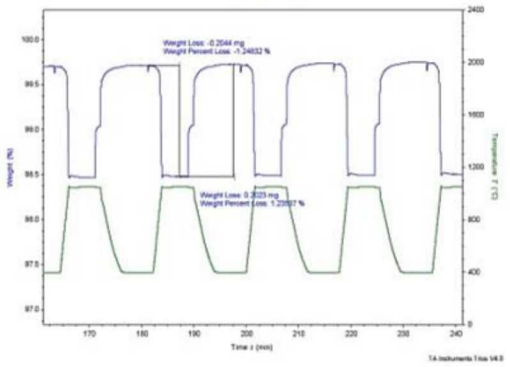


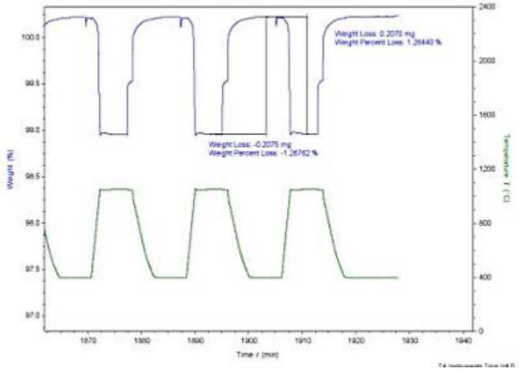




SEM of cycled particles

# 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