ETH zürich

# Perovskites for solar-to-fuel conversion

Frontiers in Energy Research


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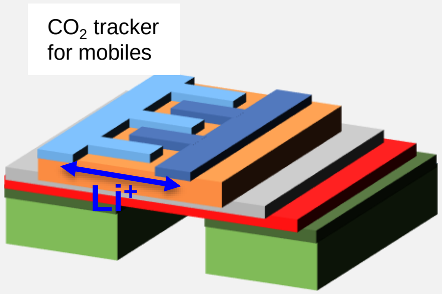
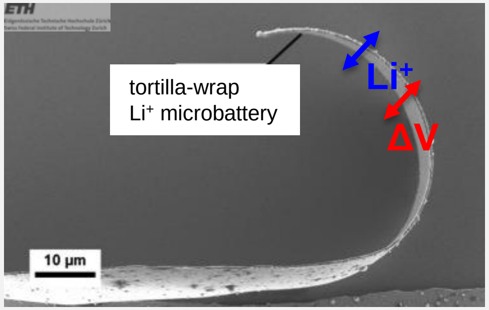
# Research in the Group of Electrochemical Materials

## Novel solid state batteries + sensors

$Li^+$ electro-chemo-mechanic devices

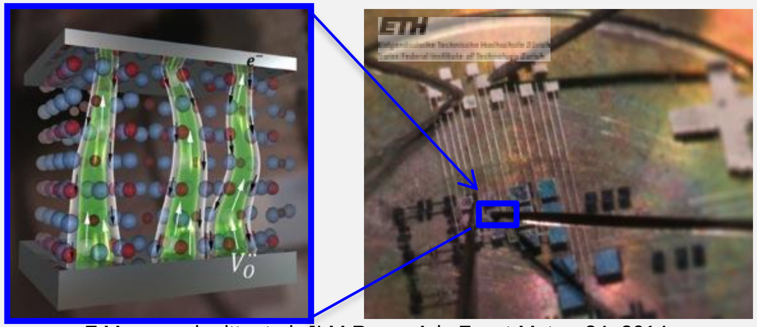



S Afyon, JLM Rupp, Adv. Energy Materials, in review 2015
JLM Rupp, M Streiff, patent EP 15000536.1, 2015

## Ionic memristors and logics

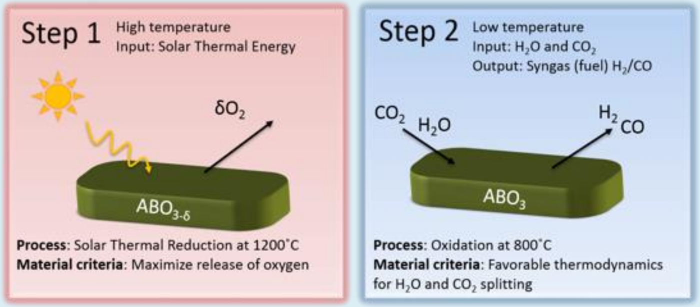
memristance and carrier kinetics at very high electric fields




F Messerschmitt, et al. JLM Rupp, Adv Funct Mater. 24, 2014
S Schweiger, et al., JLM Rupp, ACS Nano 8, 2014
F Messerschmitt et al. KLM Rupp, Adv Funct Mater, 2015

## Solar-to-fuel conversion

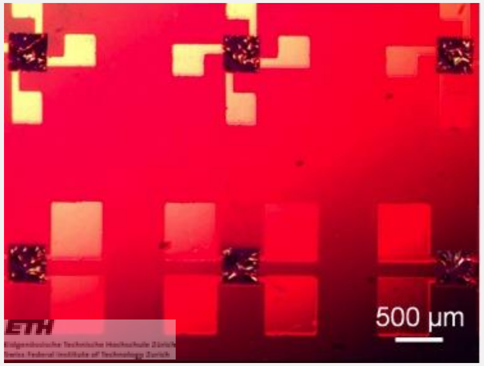
novel materials for solar-driven fuels: efficient $H_2O$ and $CO_2$ splitting




AH Bork, M Kubicek, M Struzik, JLM. Rupp, J. Mater. Chem A, in review 2015

## Micro-Energy Convertors

power: bulk and surface electro-chemistry under mechanical strain




Y Shi, AH Bork, S Schweiger, JLM Rupp, Nature Materials, in press 2015

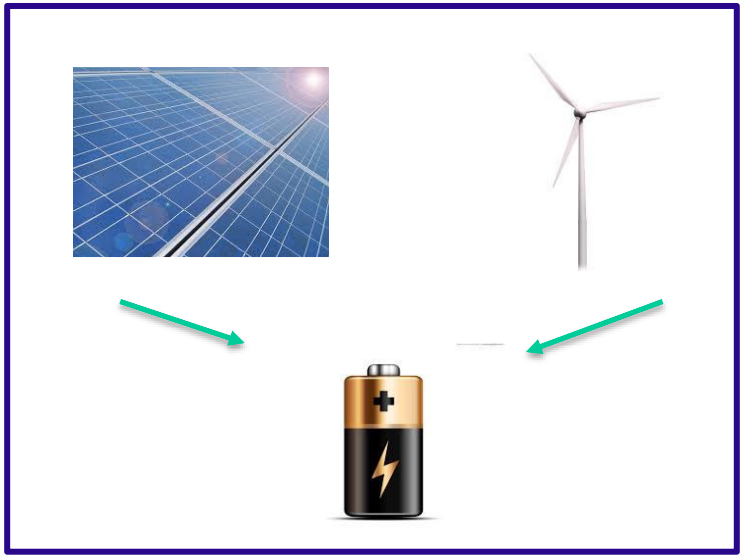
# Outline

- Introduction to Solar-to-fuel Conversion and Materials
- First results: Sr- and Co- doped $LaCrO_3$
  - Design criteria
  - Synthesis and structural characterization
  - Thermochemical fuel production
  - Stability under solar-to-fuel conditions
- Conclusions
- Outlook

My materials research!

# Introduction: Renewable Energy Conversion

Intermittent energy sources
Storage necessary



Concentrated solar power (CSP)
→ Storing solar energy in synthetic fuels

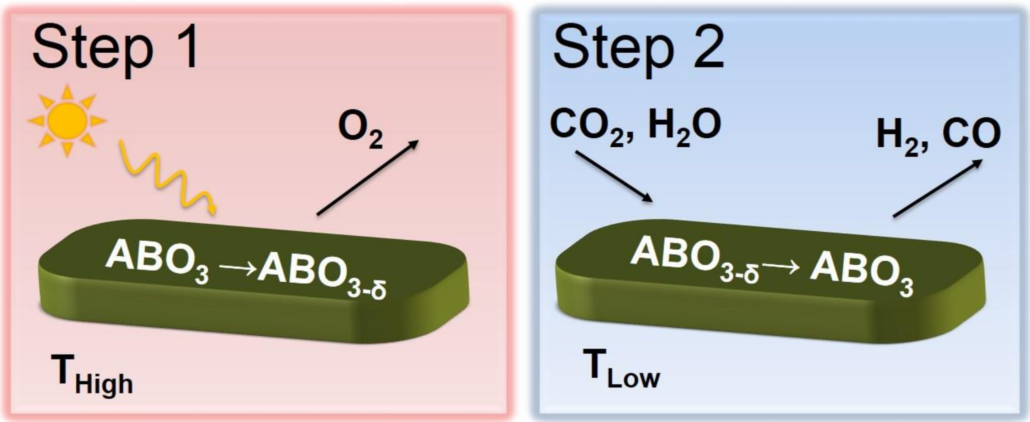
[1]

**Solar-to-fuel conversion**
- Carbon neutral renewable energy with high efficiency
- Storage of solar energy in synthetic fuels
- Round-the-clock power dispatchability

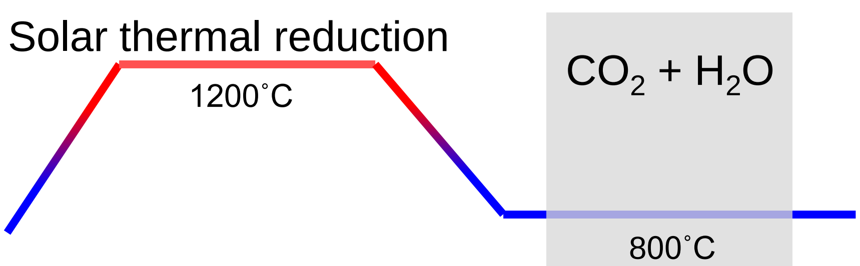
[1] Photo from: http://ciff.org/priority-impact-areas/climate/

# Introduction: Solar-to-fuel conversion

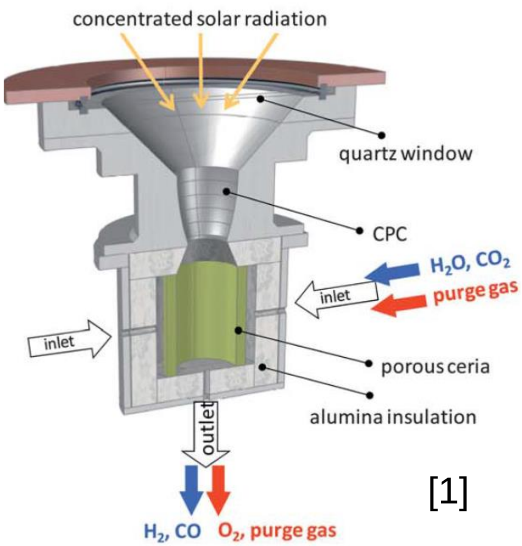
## Two-step Thermochemical Process




Energy storage in syngas/fuels

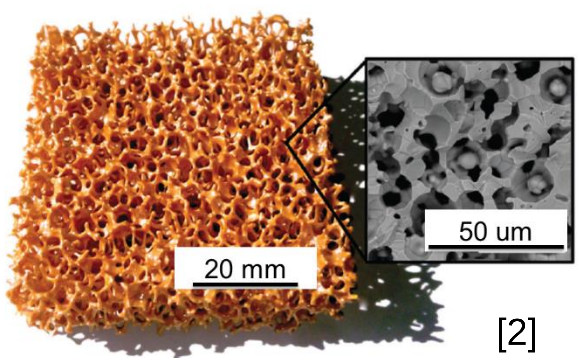



## Solar-to-fuel reactor




[1]

## Materials




[2]


[1] Romero, M, **Energy & Env. Sc**. 2012
[2] Furler P. et al. **Phys. Chem. Chem. Phys**., 2014

# Introduction: Solar-to-fuel conversion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## «Ein sensationeller Fortschritt»

Die ETH Zürich hat einen Treibstoff entwickelt, der aus Sonnenenergie gewonnen w
von der Schweizerischen Energie-Stiftung glaubt an den Durchbruch der Idee.

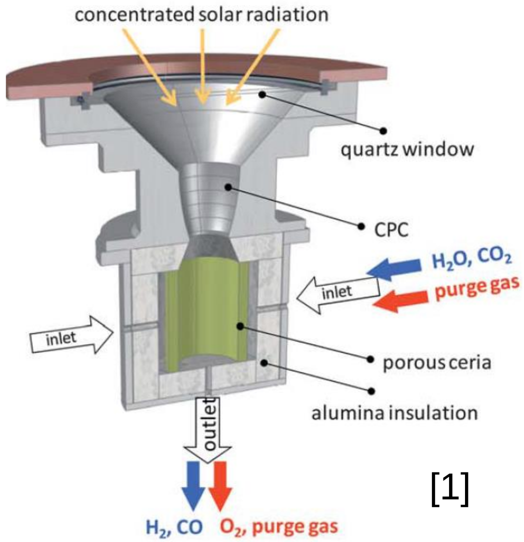
**Stichworte**

Energiepolitik

ETH Zürich

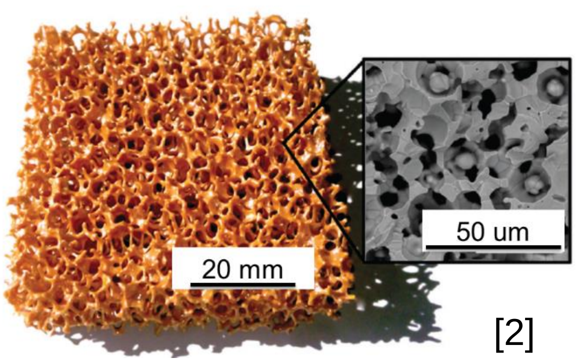


## Solar-to-fuel reactor




[1]

## Materials

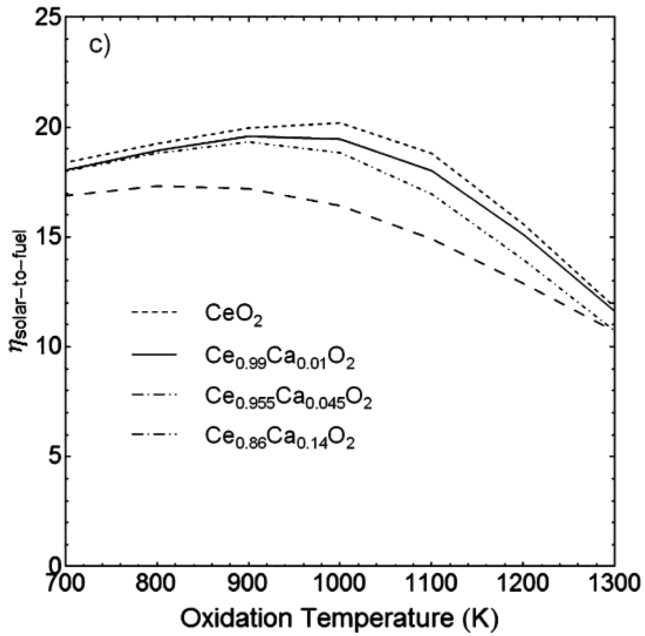



[2]

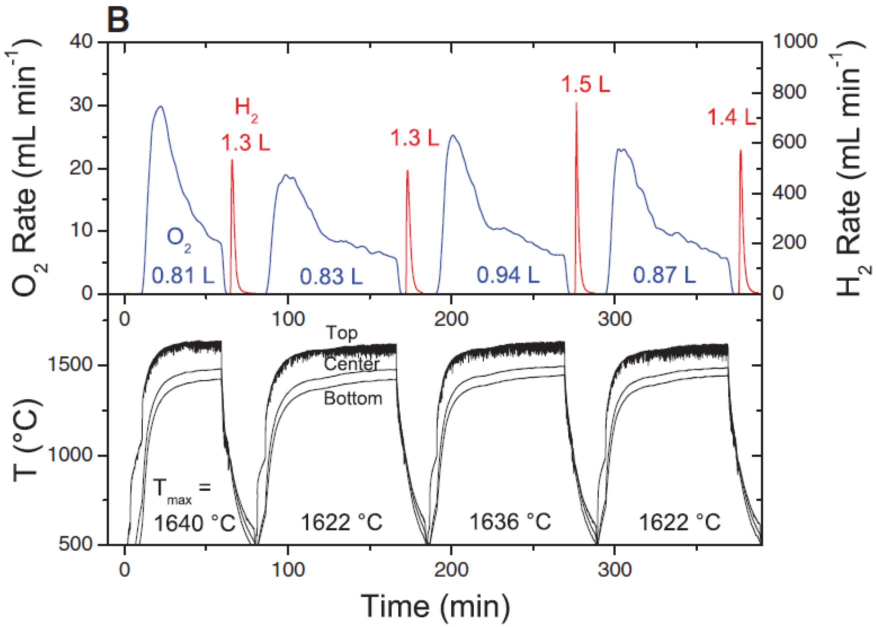

[1] Romero, M, **Energy & Env. Sc**. 2012
[2] Furler P. et al. **Phys. Chem. Chem. Phys**., 2014

# Introduction: State-of-the-art

## State-of-the-art: Ceria




Theoretical Efficiency, $\eta_{solar}$, 16-20% [1]




Reactor efficiency, 500cycles, $\eta_{solar} = 0.7\%$ [2]

**Ceria**

- Doping has limited effect on efficiency → limited oxygen storage capacity
- High temperature required for reduction → at 1500° C


[1] Scheffe, J et al. **Energy Fuels** 2012
[2] Chueh, W et al. **Science** 2010

# Introduction to Solar-to-fuel conversion

## Material Science

- **$Fe_2O_3$, ZnO [1-4]**

→ High volatility
→ Low oxygen storage capacity

- **$Ce_{1-x}B_xO_2$, B=Zr,Y,Gd,Ca [5-6]**

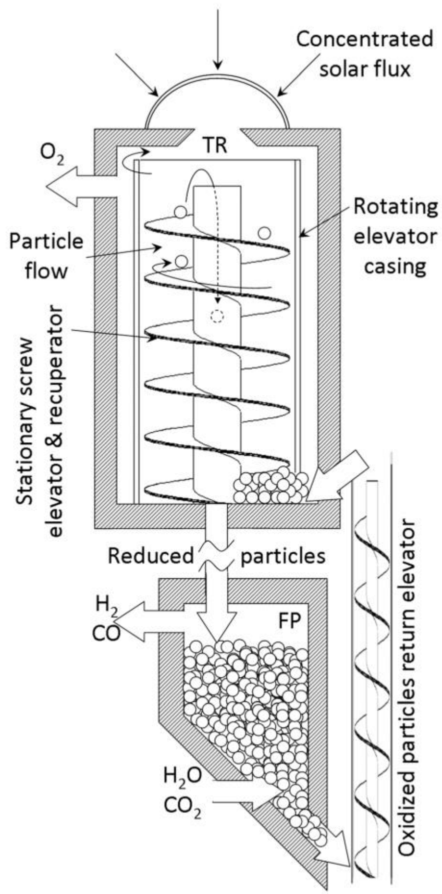
→ Doping not an option to better oxygen storage capacity
→ Too high reduction temperature

**First Perovskites:**

- **Sr- and Mn-doped $LaAlO_3$, LSMA [7]**
- **A-site doped $La_{1-x}A_xMnO_3$ with Ba, Sr, Ca[8]**

→ Promising Performance
→ DFT define optimum range $E_v$=1.8-2.4eV for LSMA at 1000-1350˚C [9]

## Mechanical Engineering




[10]

**Requirement of higher efficiency**

Materials search
My work!

[1] A. Stamatiou et al., *Chem Mater* **2010** [2] A. Weidenkaff et al., *Thermochemica Acta* **2000**, [3] C. Perkins, P. Lichty and A. W. Weimer, Chem Eng Sci 5952 (2007) [4] R. Müller et al., *Chem Eng Sci* **2008** [5] S. Abanades et al. *J. Mater. Sci*. **2010** [6] P. Furler et al. *Energy & Environmental Science* **2012**, [7] McDaniel, A, *Energy and Env. Sc.* **2013,** [8] S. Dey et al. *J. Phys. Chem.* 2015**,** [9]A.M. Deml et al. *Chem. Mater.* 2014 [10] I. Ermanovski et al. *J. of Solar Energy Eng.* **2013,**

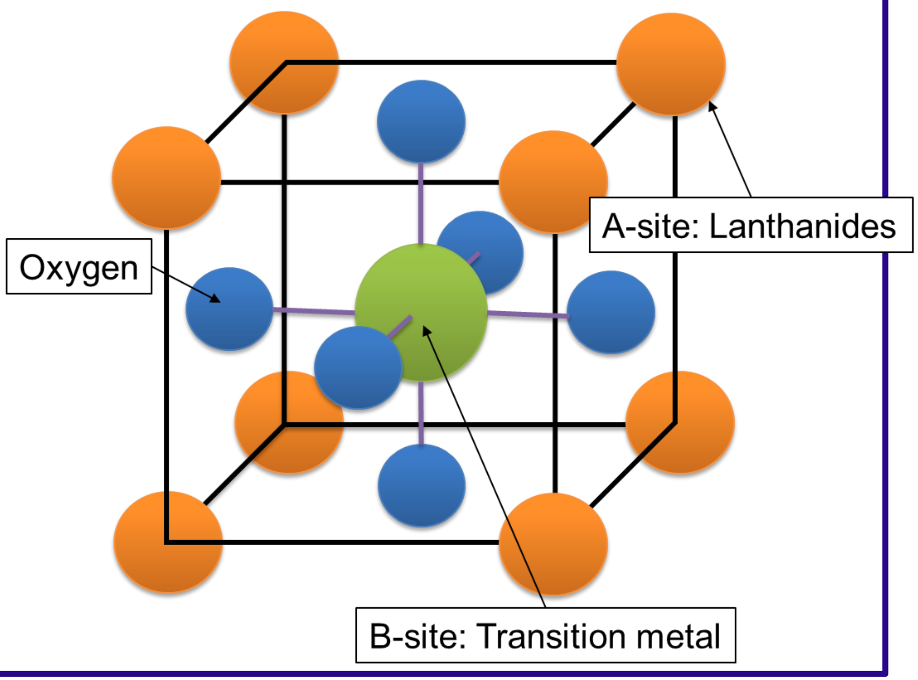
# Introduction to Solar-to-fuel conversion

## How do we improve efficiency?

**Investigate perovskites**

- Highly redox active
- High degree of flexibility in doping
- Lowered operation temperature

### Perovskites: $ABO_3$




**Why perovskites?**

Redox activity
Reduces at low temperature
Potential for efficiency increase

# Outline

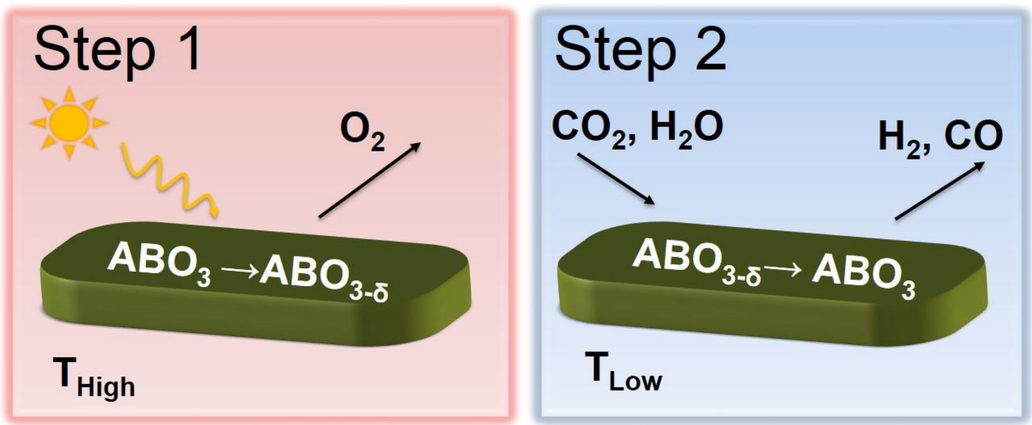
- Introduction to Solar-to-fuel Conversion and Materials
- First results: Sr- and Co- doped $LaCrO_3$
  - Design criteria
  - Synthesis and structural characterization
  - Thermochemical fuel production
  - Stability under solar-to-fuel conditions
- Conclusions
- Outlook



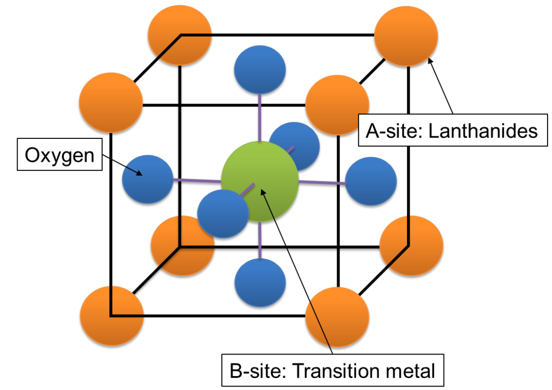
My work!
In materials research

# Design Criteria

## Two-step Thermochemical Process




Energy storage in syngas/fuels



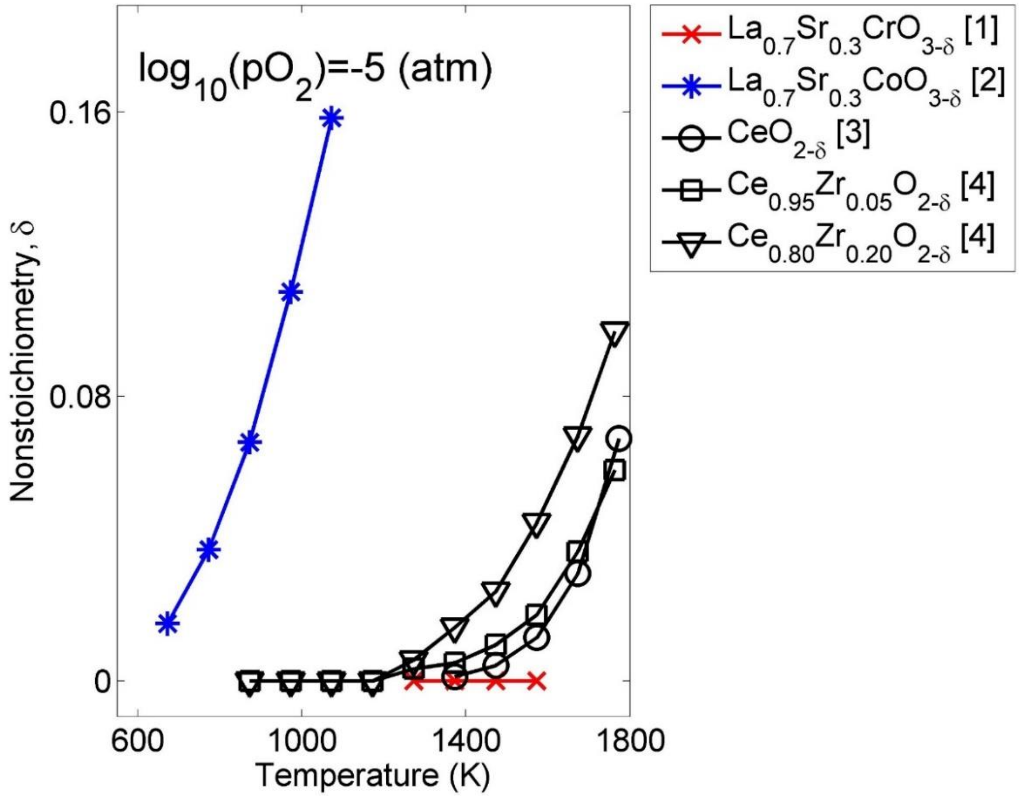

## Novel solid solution series $La_{0.6}Sr_{0.4}Cr_{1-x}Co_xO_{3-\delta}$

- Acceptor doping on A-site with strontium to increase maximum non-stoichiometry
- Vary B-site doping to tailor thermodynamic properties for optimum fuel yield

**Design criteria** Step 1: High release of oxygen
Step 2: Favorable thermodynamics for water and $CO_2$ splitting

# Literature: Redox Properties

**B-site doped $(La,Sr)BO_3$ and ceria**

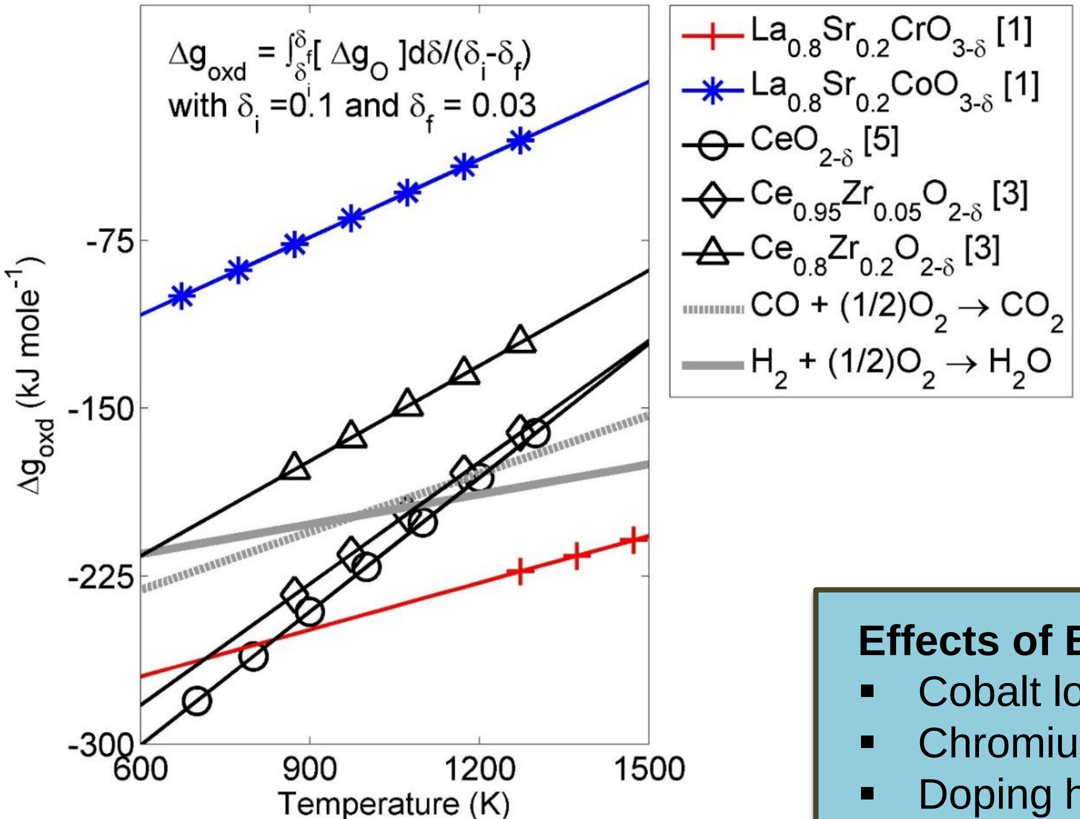



- Cobalt lowers reduction temperature$T_{high}$ (from 1000˚C down to 600 ˚C)
- Chromium increases $T_{high}$
- Doping has larger effect on perovskites compared to ceria


[1] Mizusaki et al. *J Solid State Chem* **1984** [2] Mizusaki et al. *J Solid State Chem* **1989**
[3] Kuhn et al. *Acta Materialia* **2013**, [4] Hao et al. *Chem. Mater.* **2014**

# Literature: Thermodynamics

## Gibbs free energy of oxidation for B-site doped (La,Sr)$BO_3$ and ceria




$$H_2O(g) + \frac{1}{\delta} MO_{2-\delta} \rightarrow \frac{1}{\delta} MO_2 + H_2(g)$$

$$\Delta g_{rxn} = \Delta g_{oxd} - \Delta g_{H_2O}$$

**Effects of B-site doping in perovskite**

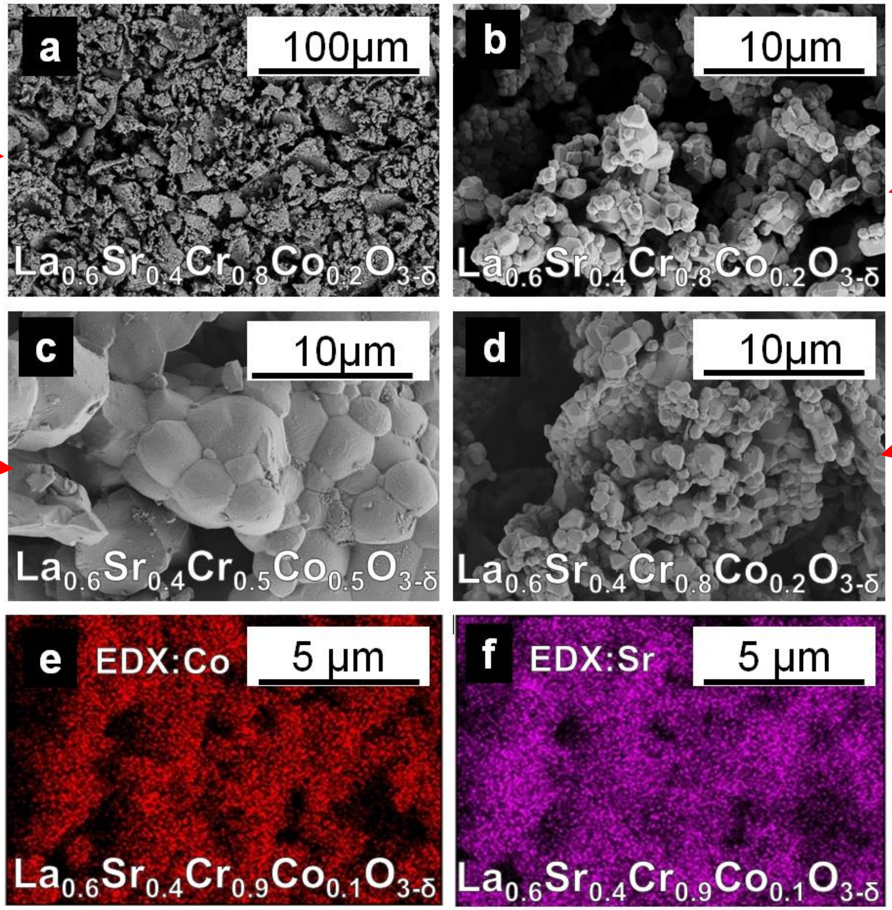
- Cobalt lowers $\Delta g_{oxd}$ (less negative)
- Chromium increases $\Delta g_{oxd}$ (more negative)
- Doping has larger effect on perovskites compared to ceria


[1] Mizusaki et al. *J Solid State Chem* **1984** [2] Mizusaki et al. *J Solid State Chem* **1989,** [3] Kuhn et al. *Acta Materialia* **2013**, [4] Hao et al. *Chem. Mater.* **2014**, [5] Scheffe, J et al. *Energy Fuels* **2012**

# Making New Solar-to-Fuel Perovskites

Particle size

High cobalt content leads to grain growth

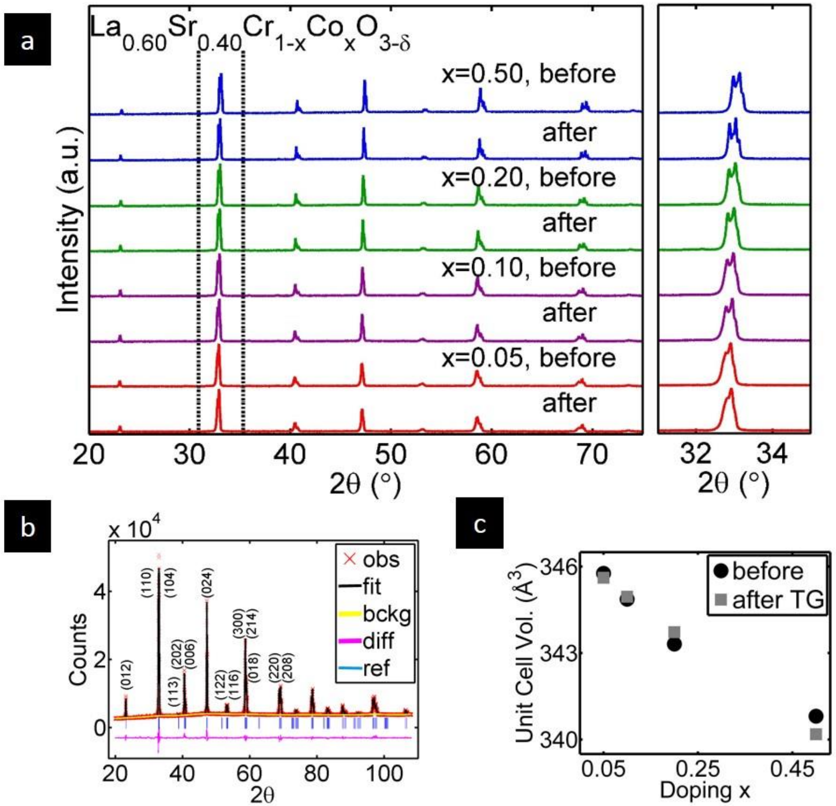



Before

After

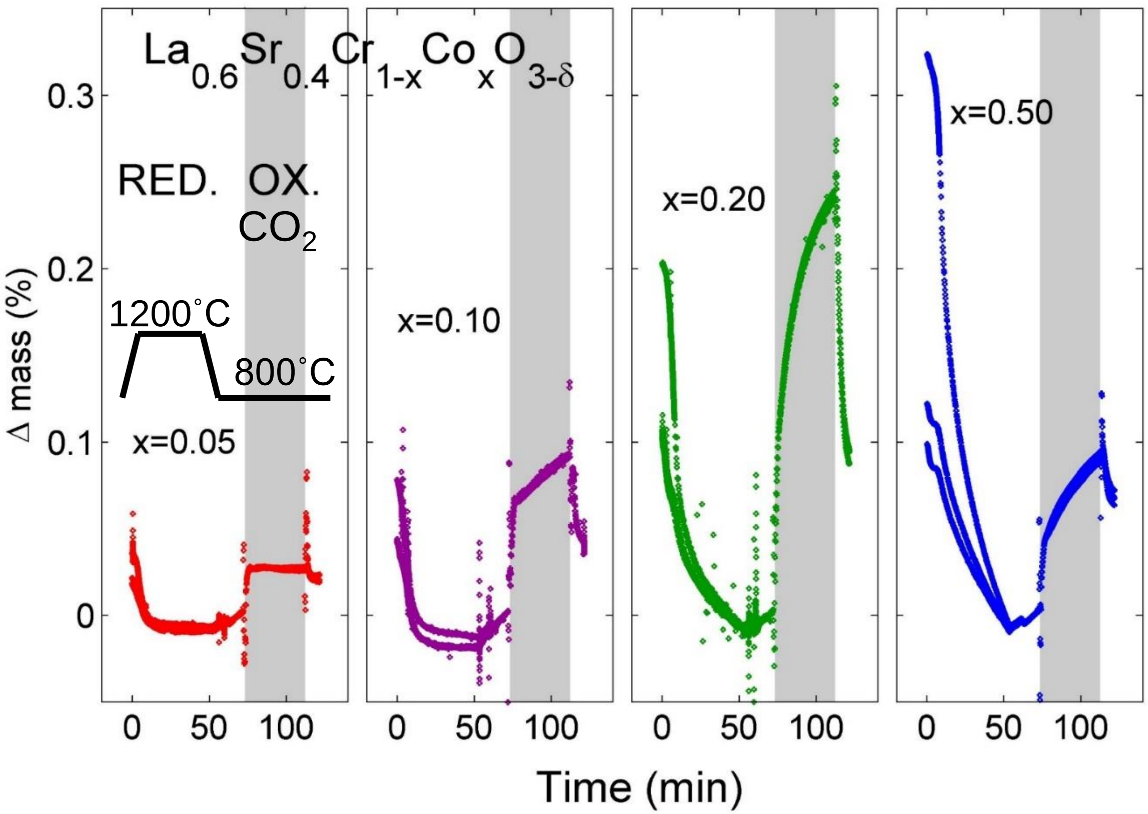
- Successful synthesis of $La_{0.6}Sr_{0.4}Cr_{1-x}Co_xO_{3-\delta}$, for x=0.05, 0.10, 0.20, 0.50
- Homogeneous distribution of metal cations
- Stable during thermochemical cycling

# Structural Analysis




- Succesful synthesis of $La_{0.6}Sr_{0.4}Cr_{1-x}Co_xO_{3-\delta}$, for x=0.05, 0.10, 0.20, 0.50
- Stable during thermochemical cycling

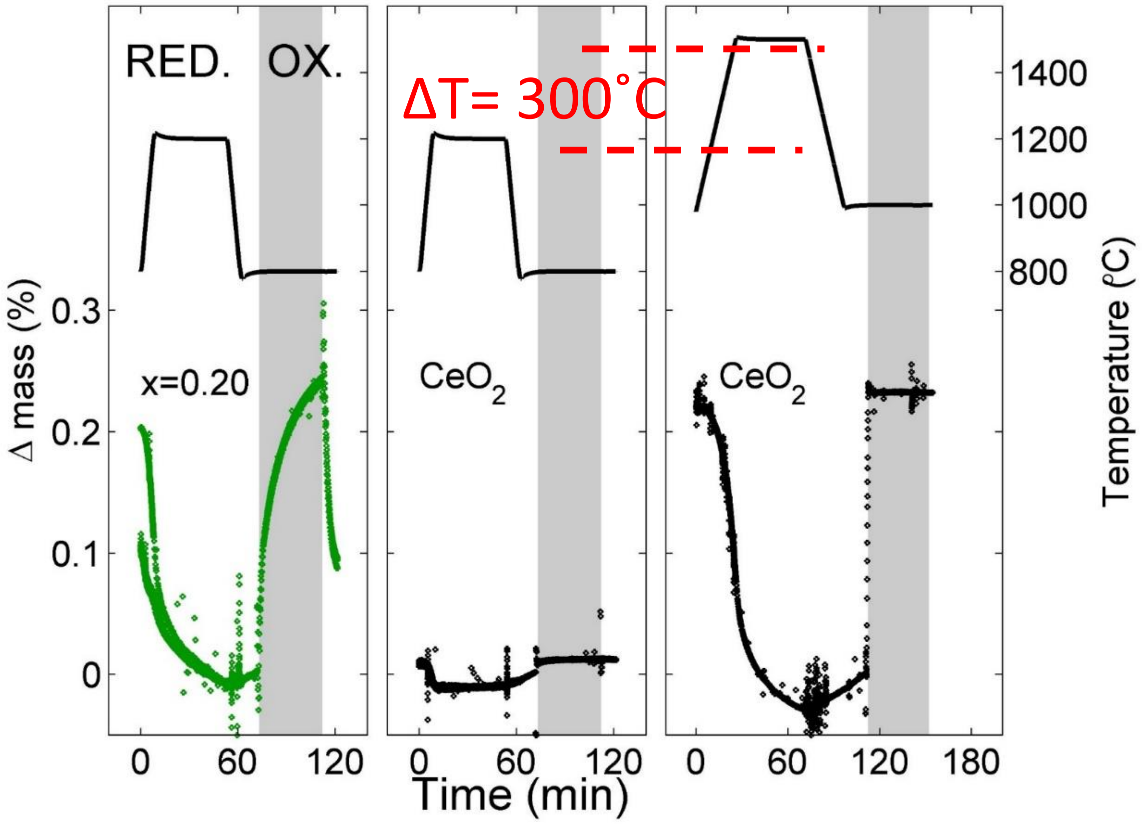
# Solar Thermochemical Fuel Production




**Cycling**
$T_{reduction}$= 1200˚C
$T_{re\text{-}oxidation}$= 800˚C

- High tuneability! Fuel production is 10x greater for x=0.20 compared to x=0.05.
- Optimum in fuel production for x=0.2
- Temperature operation for reactor is potentially lowered by 300˚C!

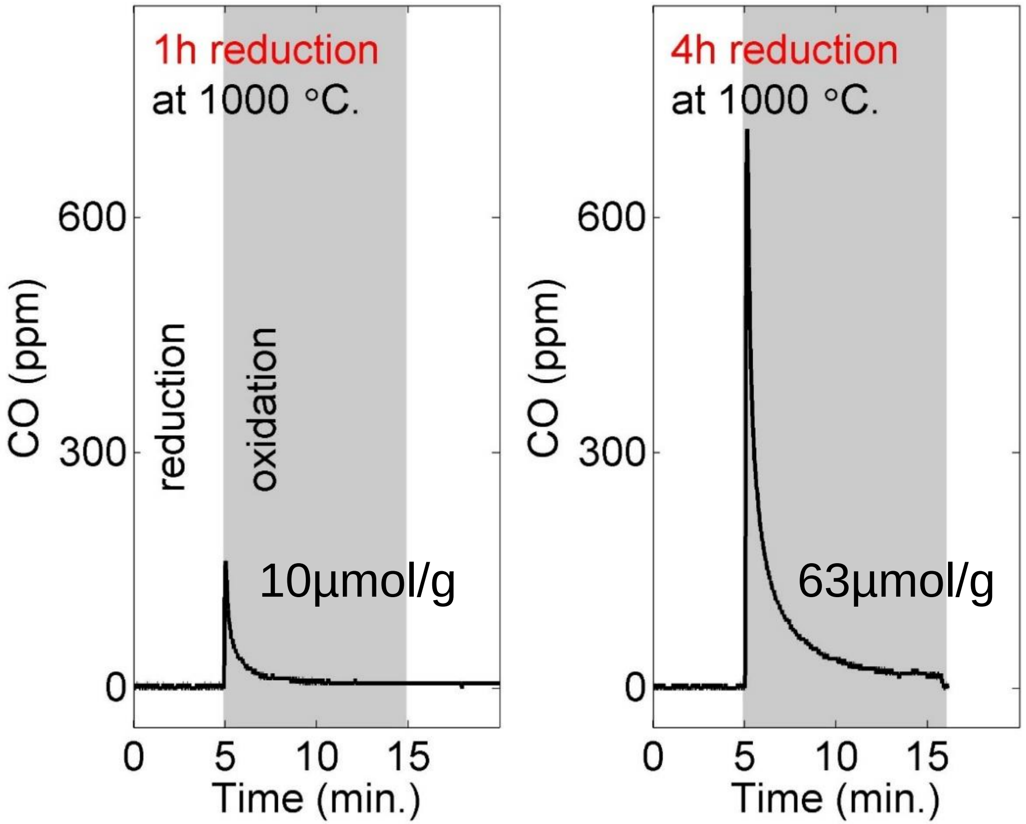
# Fuel Production: Comparison to State-of-the-art




$La_{0.6}Sr_{0.4}Cr_{0.8}Co_{0.2}O_{3-\delta}$ and ceria

- 25x greater CO production for thermochemical cycling at 800-1200 ˚C
- Same fuel yield for 300 ˚C lowered operating temperature compared to state-of-the-art ceria

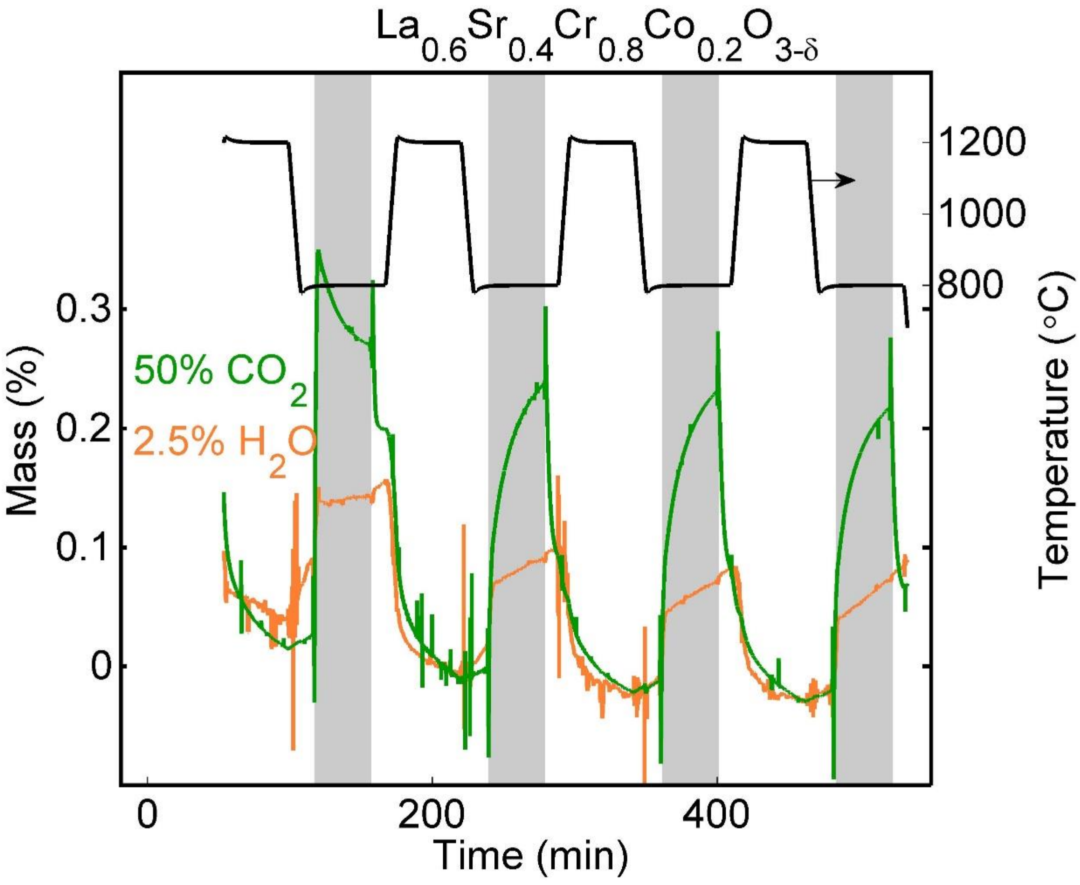
# Fuel Production: Verification




Fluidized bed reactor with infrared sensors -collaboration with Prof. Christoph Müller (ETHZ)

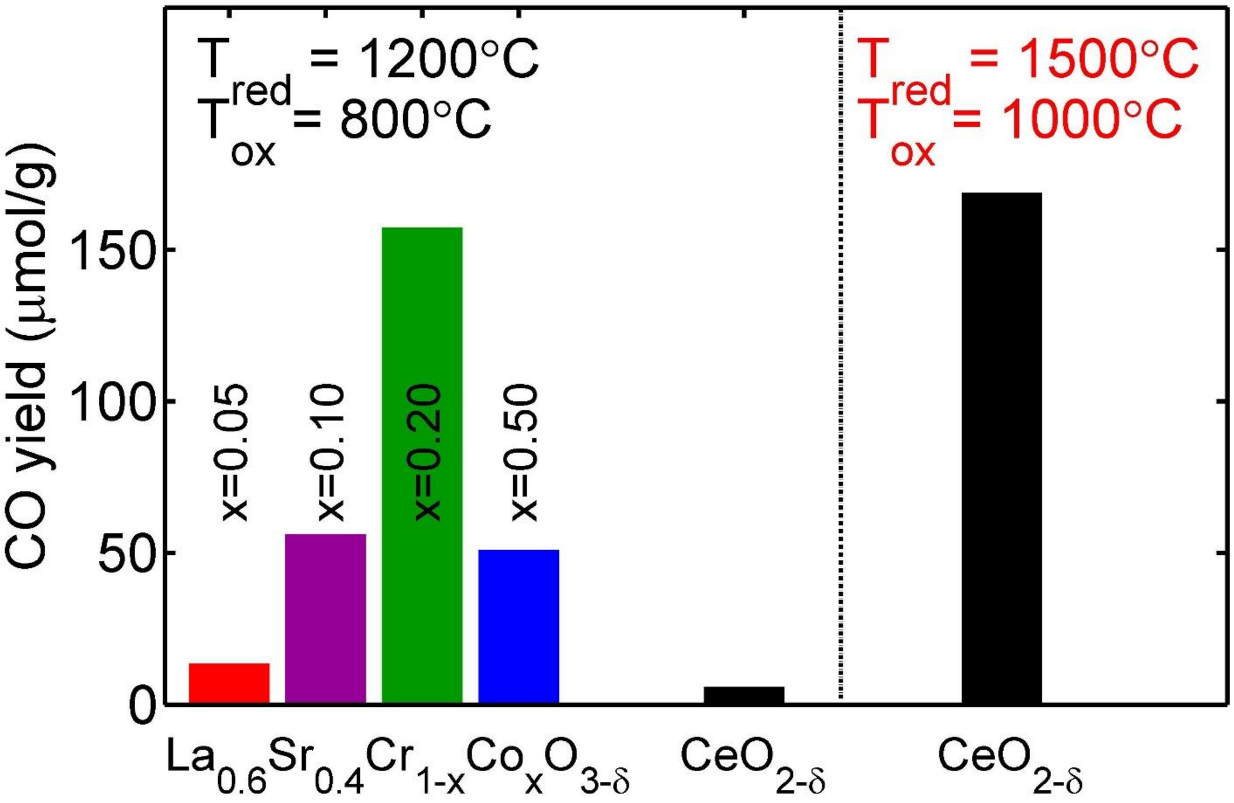
- Verification of $CO_2$ splitting
- Fast re-oxidation in this fluidized bed reactor

# Water and $CO_2$ splitting




The new proposed perovskite $La_{0.6}Sr_{0.4}Cr_{0.8}Co_{0.2}O_{3-\delta}$ splits both $H_2O$ and $CO_2$

# Solar Thermochemical Fuel Production

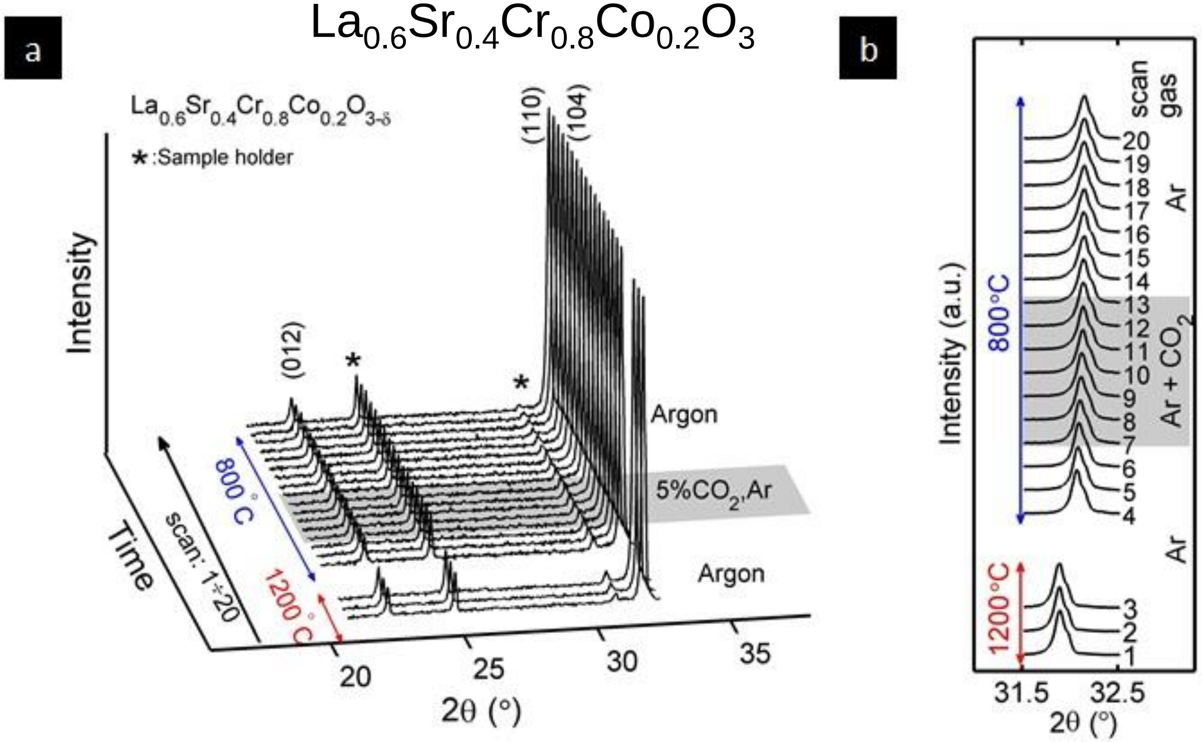



CO production is 157μmol/g for x=0.20 for new perovskite composition compared to 169 μmol/g for ceria at a 300 ˚C higher temperature !

# In-situ XRD, re-oxidation with $CO_2$

Carbonates formation in $La_{0.6}Sr_{0.4}CoO_3$ when exposed to $CO_2$[1,2]

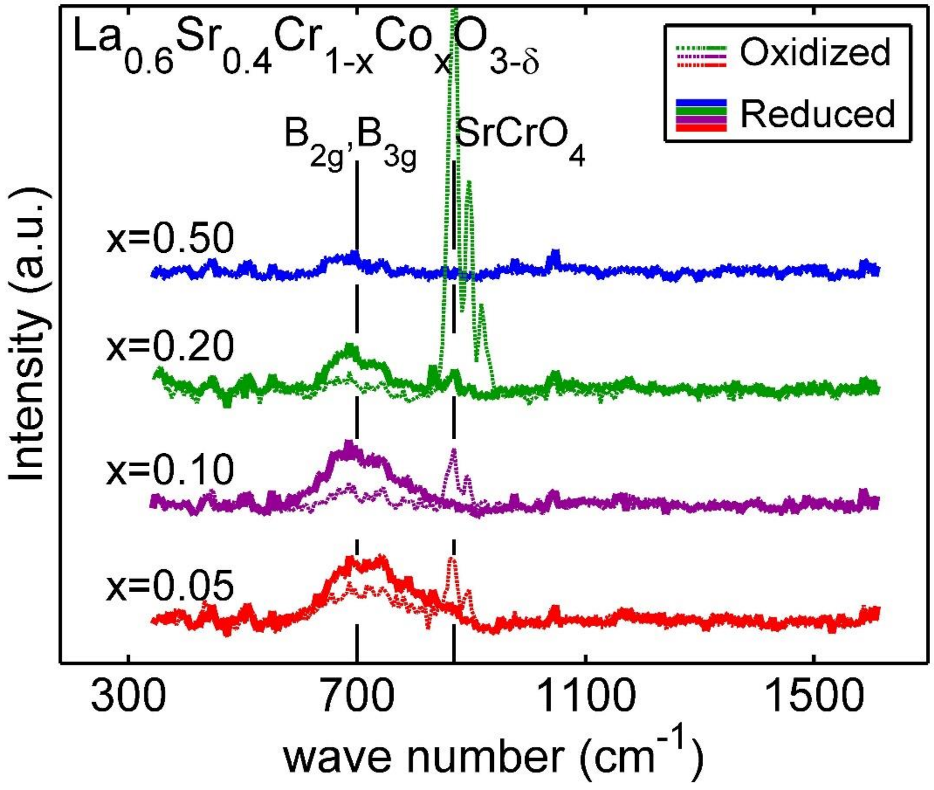
$La_{0.6}Sr_{0.4}Cr_{0.8}Co_{0.2}O_3$




$La_{0.6}Sr_{0.4}Cr_{0.8}Co_{0.2}O_3$ is chemically stable in $CO_2$
i.e. no carbonate formation are detectable in in-situ XRD


[1] Esposito, V. et al. *Solid State Ionics* **2012**
[2] Rajesh, S. et al. *Electrochemica Acta* **2014**

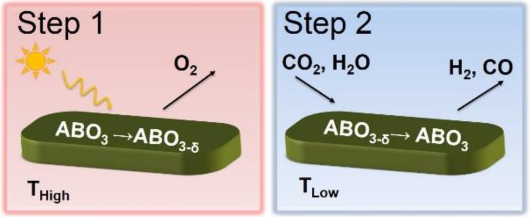
# Near Order Raman Characteristics




$B_{2g}/B_{3g}$ bending mode at 700cm$^{-1}$

- Surface impurity phase $SrCrO_4$ dissappears after thermochemical cycling
- Possible correlation between $\Delta g_{oxd}$ and force constant
- No adverse carbonates present

# Conclusions




1. Design criteria
   → Proven generality for perovskites as model system

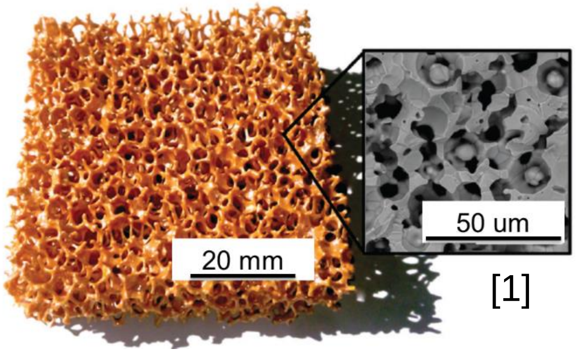
2. Characterization by XRD, SEM and Raman Near Order
   → Single phase material with high stability in thermochemical cycling

3. Thermochemical Fuel Production
   → Cr- and Co-doping can be used to optimize fuel production far beyond state-of-the-art material Ceria !
   → High fuel yields at 300˚C lowered temperature
   → 25x higher CO yield at 800-1200˚C (compared to ceria)

→ A new solar-to-fuel conversion material proposed with high performance and degree of tunability!

# Outlook

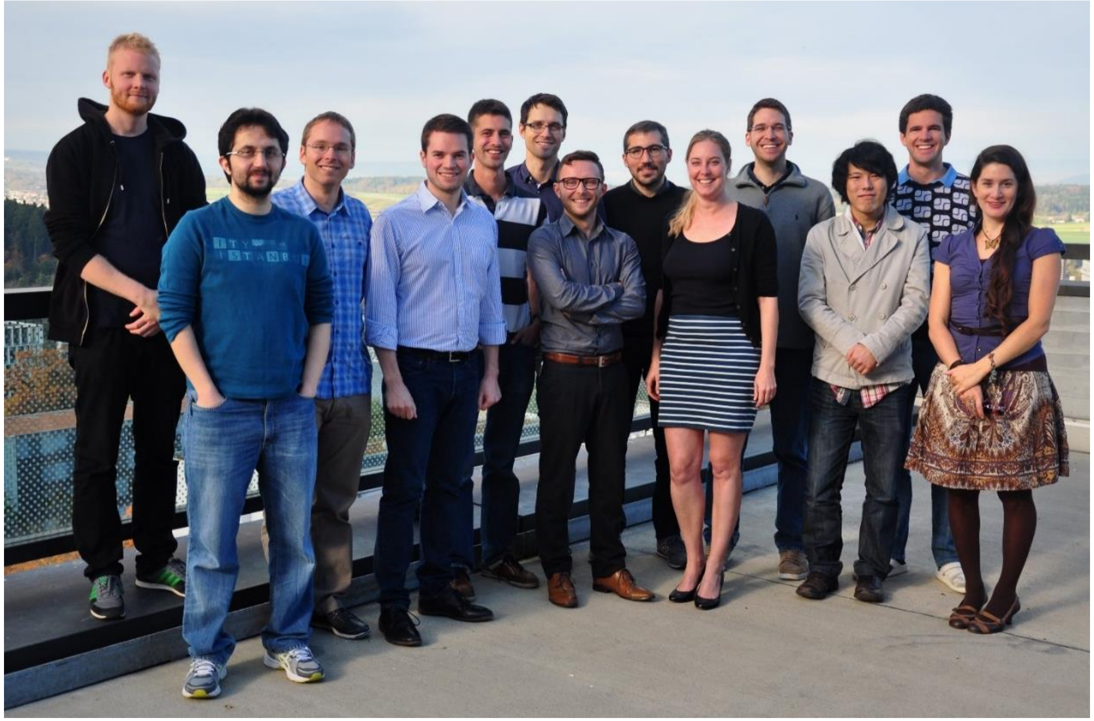
- Further investigation of $La_{0.6}Sr_{0.4}Cr_{1-x}Co_xO_{3-\delta}$, i.e. real system tests, oxidation state changes
- Defect model of $La_{0.6}Sr_{0.4}Cr_{1-x}Co_xO_{3-\delta}$
- Additional perovskites
    - $BaZr_{0.8}BO_{3-\delta}$, with B=Cr, Co, Fe, Mn.
    - $(La,Sr)BO_{3-\delta}$ with B=Cr, Co, Fe, Mn, Al.
- Raman spectroscopy measurements - expand design criteria
- Fluidized bed reactor to test new design rules
- Thermodynamic Efficiency
- Reticulated porous ceramics




[1]

[1] Furler P. et al. *Phys. Chem. Chem. Phys.*, **2014**

# Acknowledgement



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