Performance of $Ca_{1-x}Sr_xMnO_{3-\delta}$-Foams and -Granules in Thermochemical Oxygen Pumping

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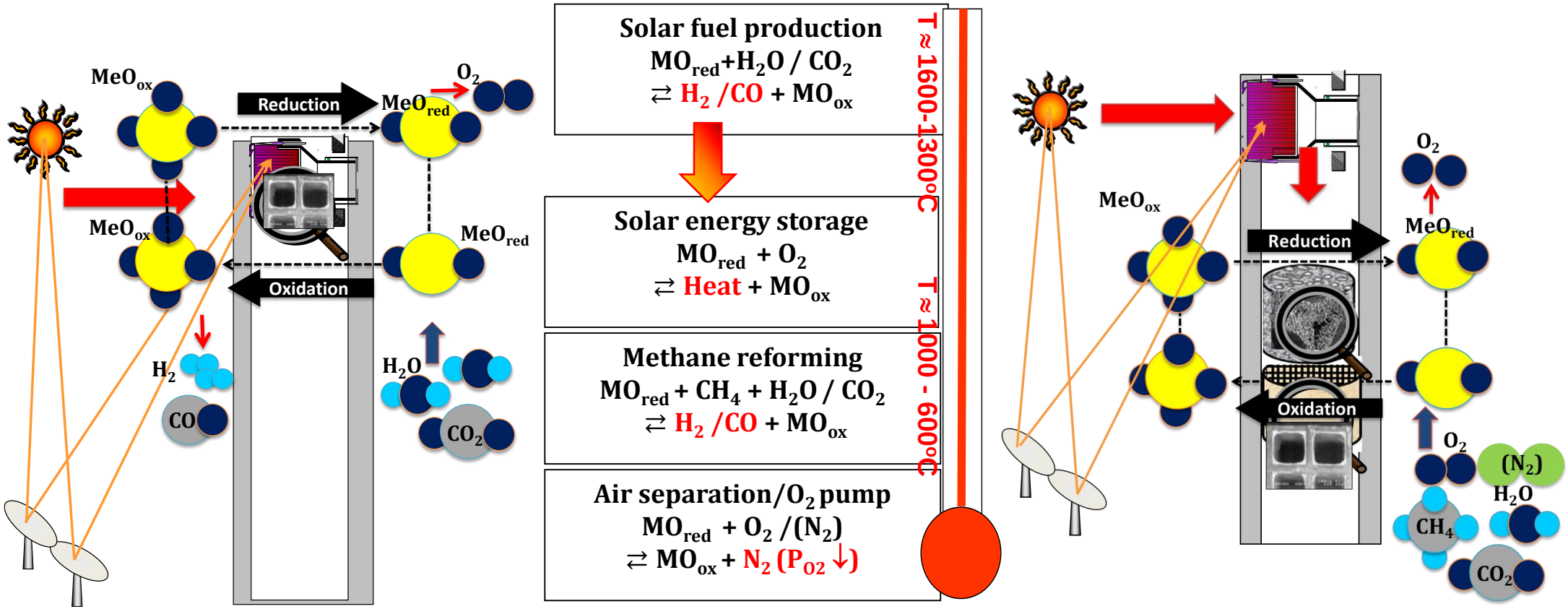
DLR

Thermochemical Energy Conversion with Metal Oxides



Based on: C. Agrafiotis et al., J. Sol. Energy Eng., 2019, 141(2): 021010

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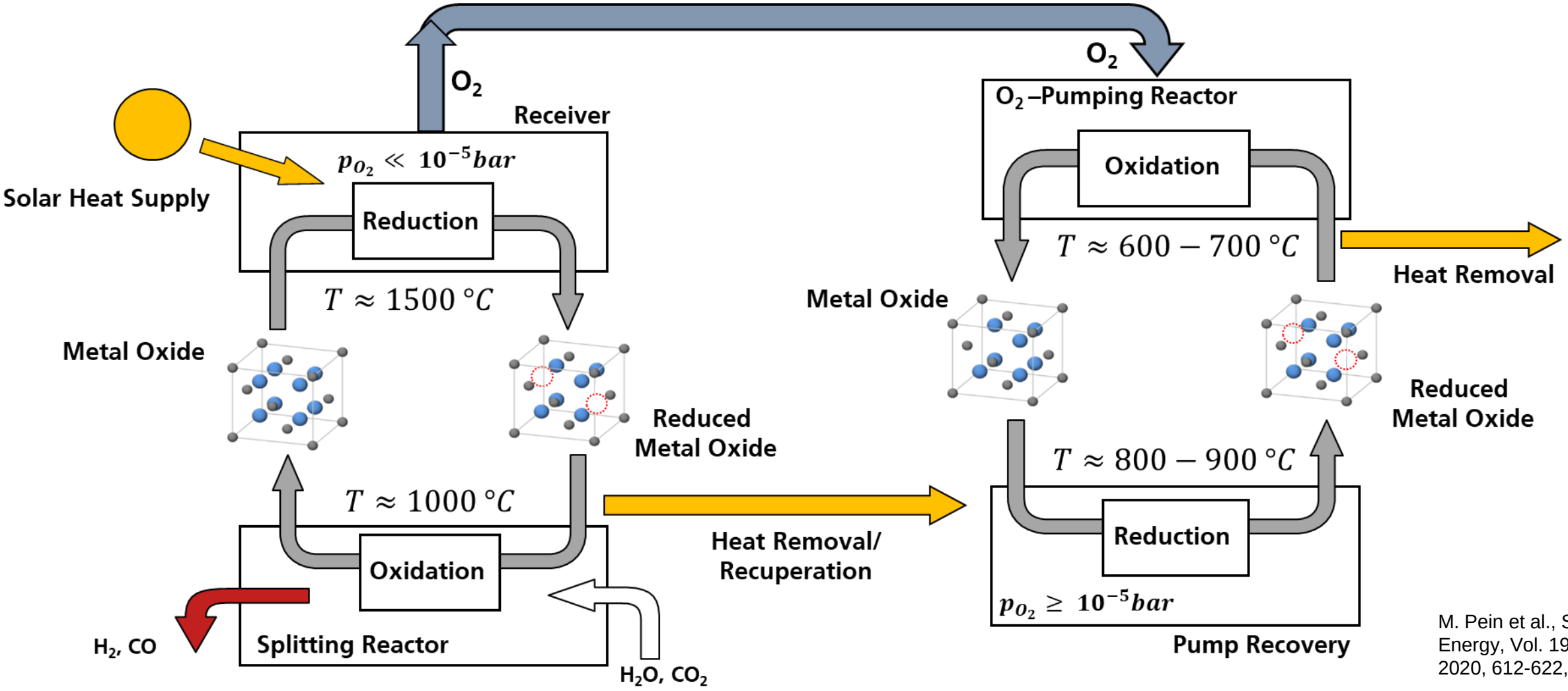
Principle of Thermochemical Oxygen Pumping in CSP



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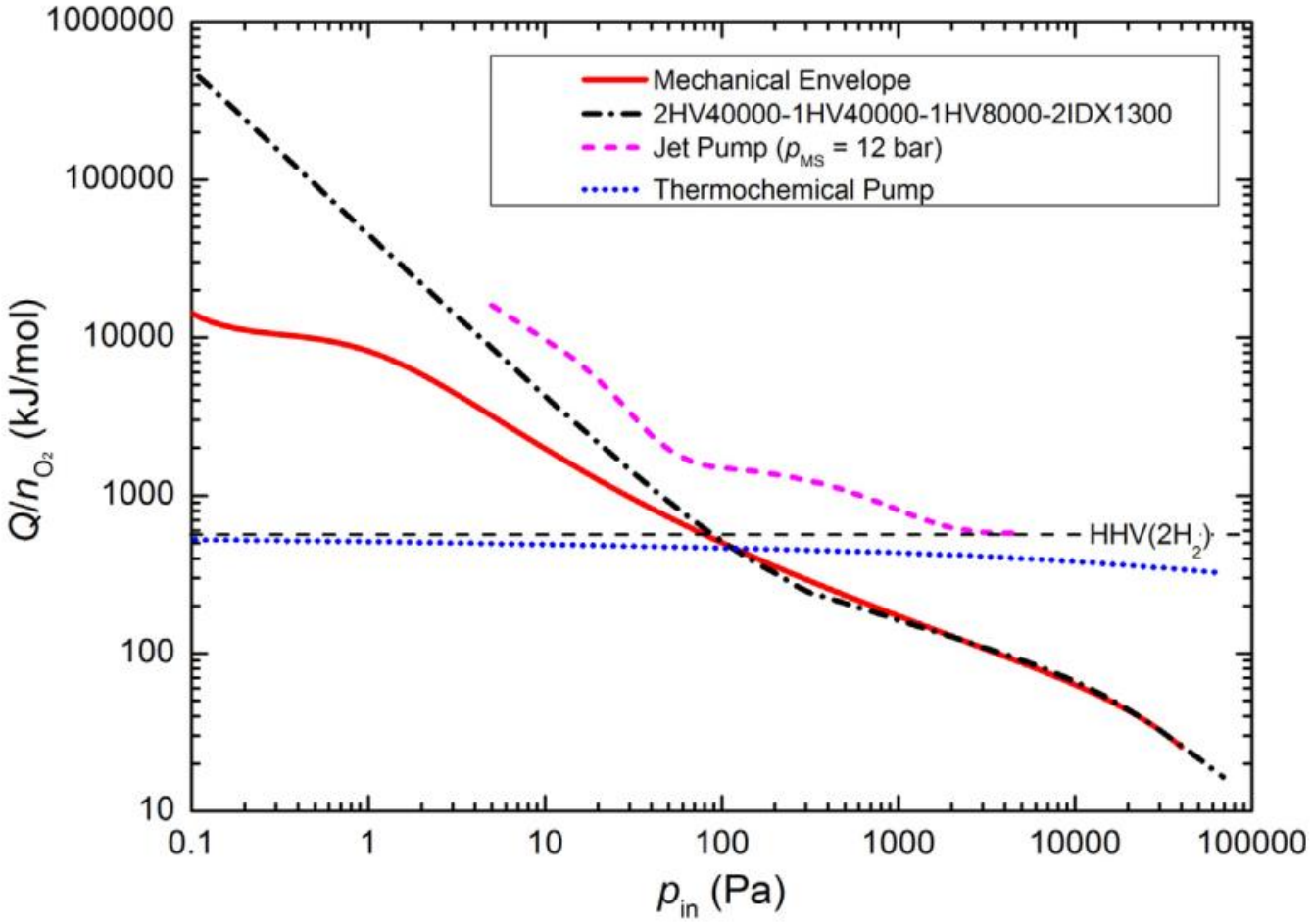
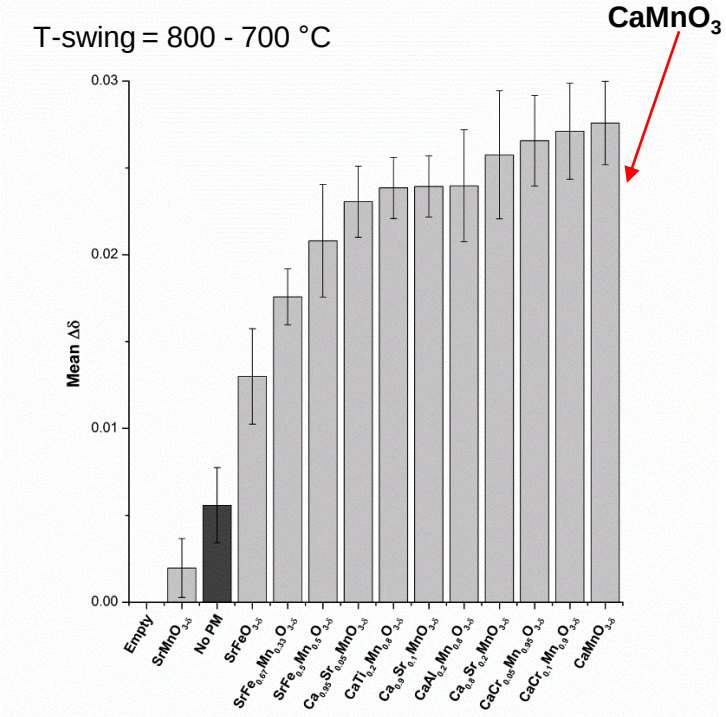
TCOP vs. Mechanical Pumping



S. Brendelberger et al., Solar Energy, Volume 141, 2017, Pages 91-102

Material Screening

- 14 compositions experimentally screened
- Powder samples
- $CaMnO_3$ performed best



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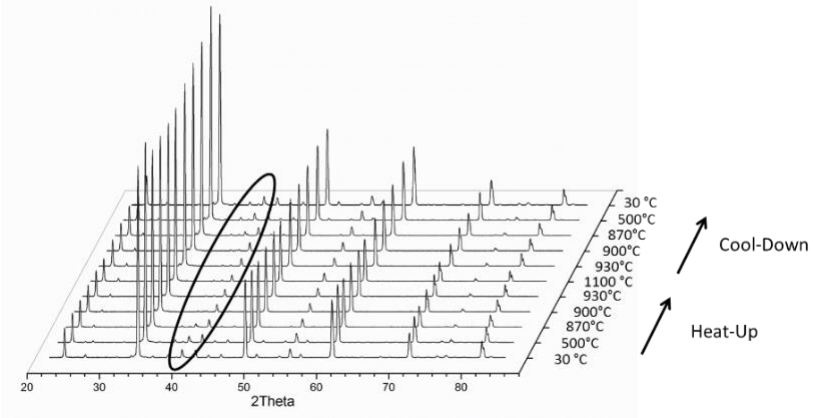
Phase transition at ~890°C



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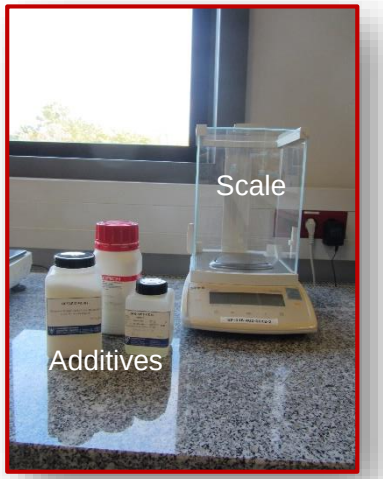
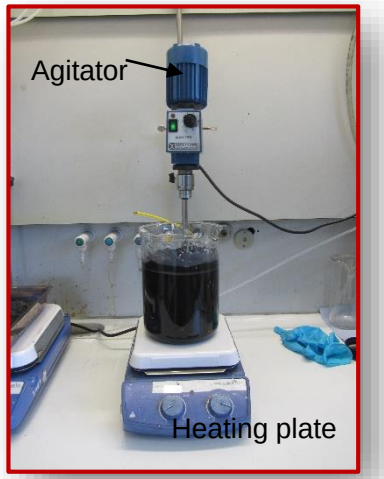
- Large influence on thermal expansion
- 5% - 10% of Sr-doping for optimized expansion behavior

L. Klaas and M. Pein et al., Phys. Chem. Chem. Phys., 2022,24, 27976-27988

RPC Fabrication Process : PU replica method



① Preparation of mixture

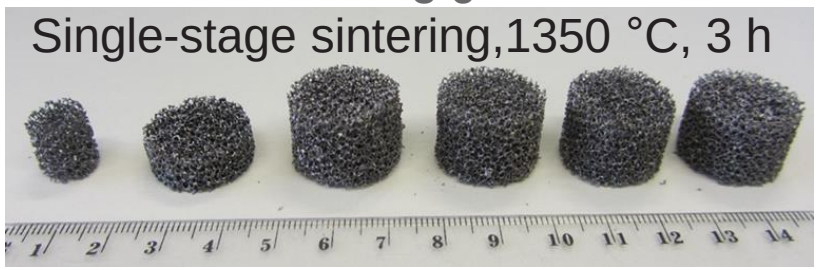


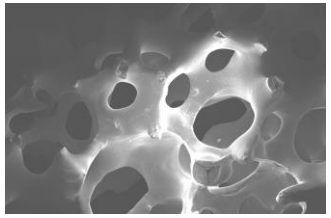
② Deflocculation

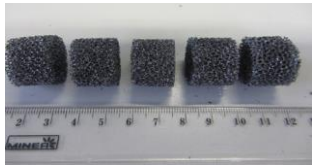
③ Coating & removal of excess slurry

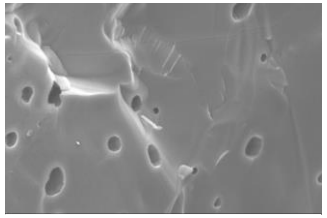
④ De-binding & Sintering

$CaMnO_{3-\delta}$ RPCs









- 30 ppi foams withstand a load of 1 bar
- Mechanically stable and easy to handle

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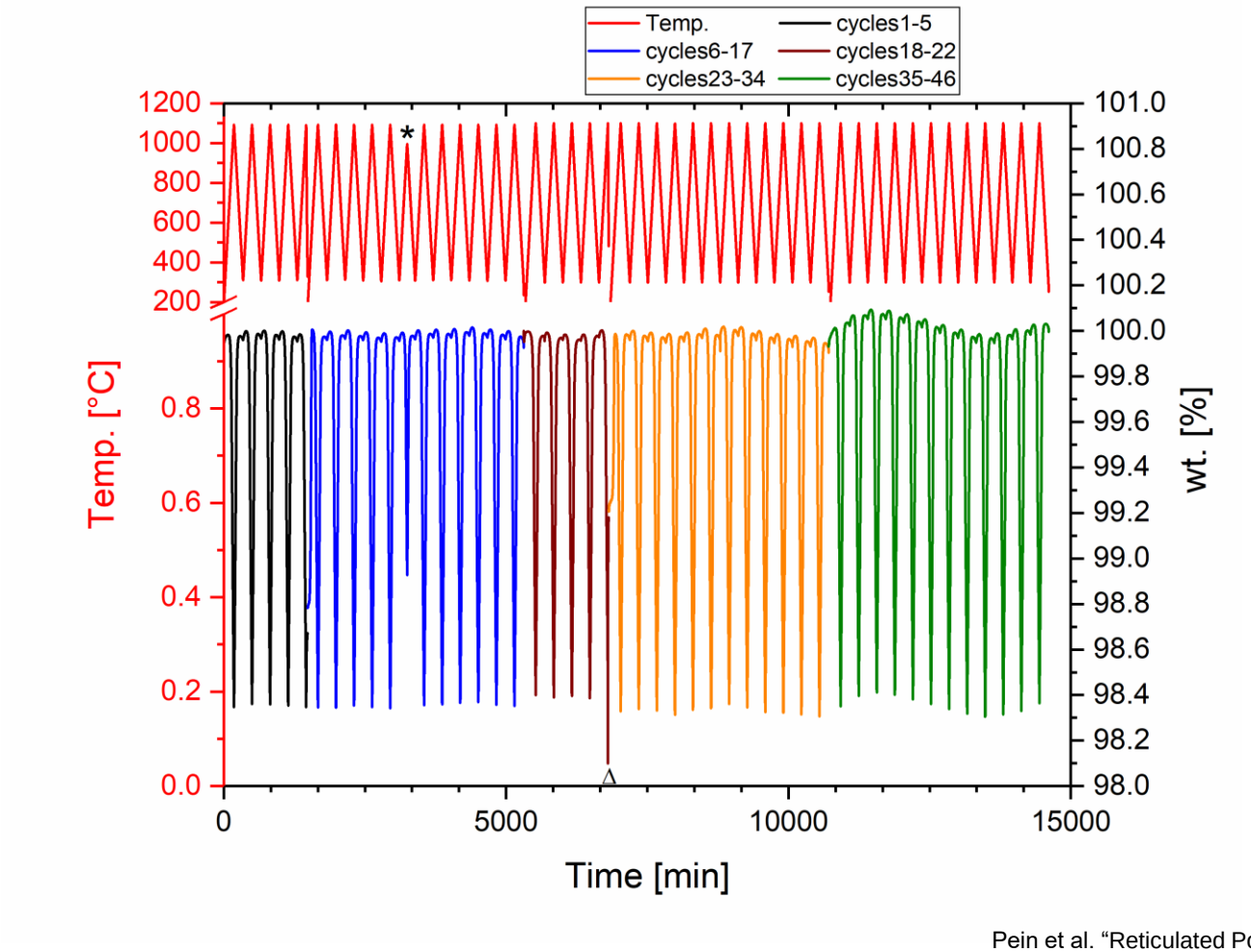
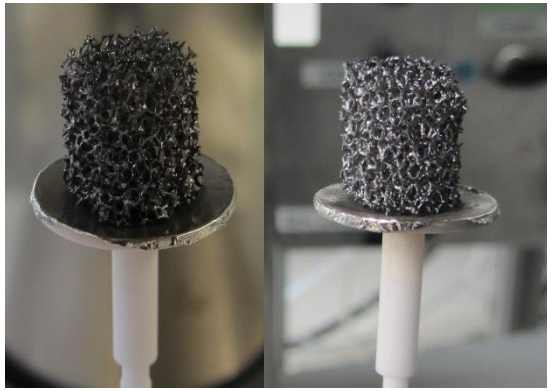
Cyclic stability of foam specimens – $CaMnO_3$



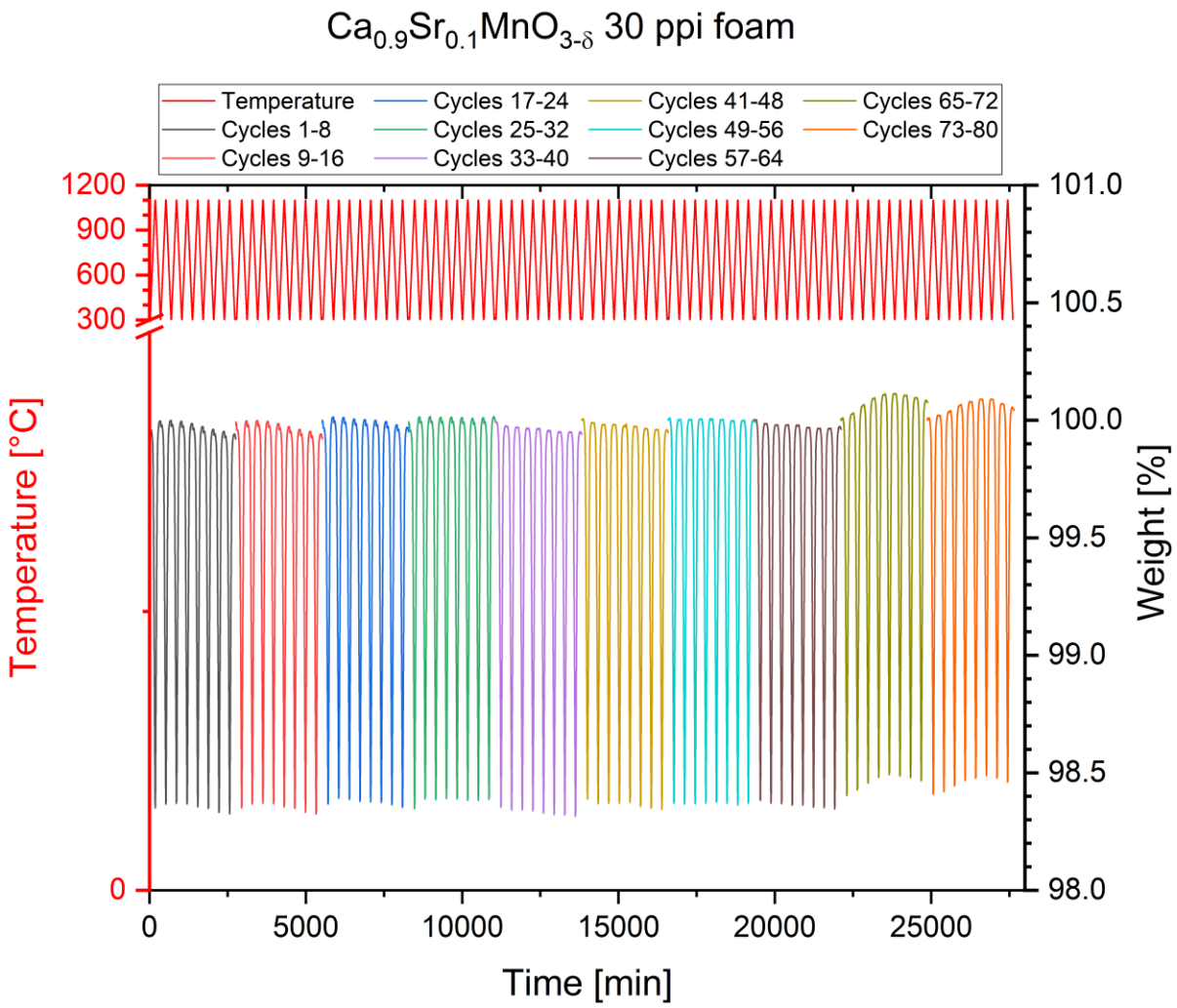


before after

- Stable thermodynamics over 46 cycles 300-1100°C
- No deformation of the foam sample

Pein et al. “Reticulated Porous Perovskite Structures forThermochemical Solar Energy Storage”, *Advanced Energy Materials* (2022), p. 2102882. DOI: https://doi.org/10.1002/aenm.202102882.

Cyclic stability of foam specimens – $Ca_{0.9}Sr_{0.1}MnO_3$



- Fully reversible reduction and oxidation over 80 cycles

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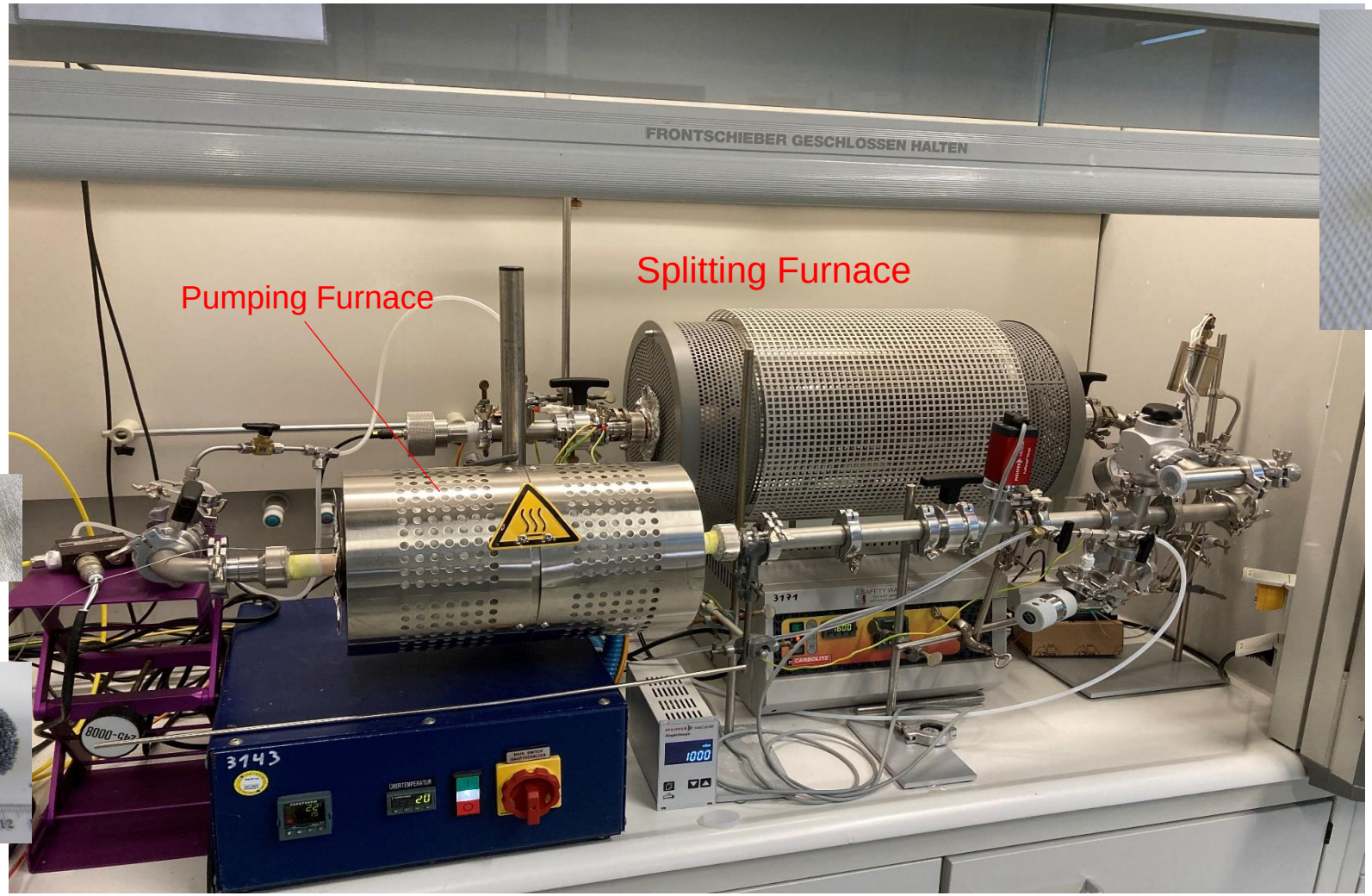
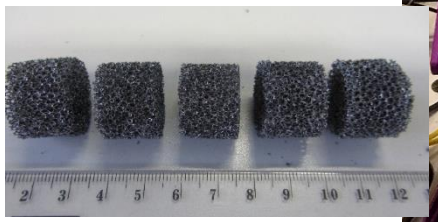
Oxygen Pumping Setup

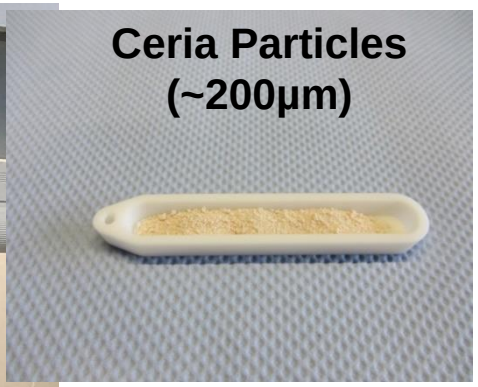


4.2g of pumping material

Granules ~1-5mm

Foams 30ppi





5g of splitting material

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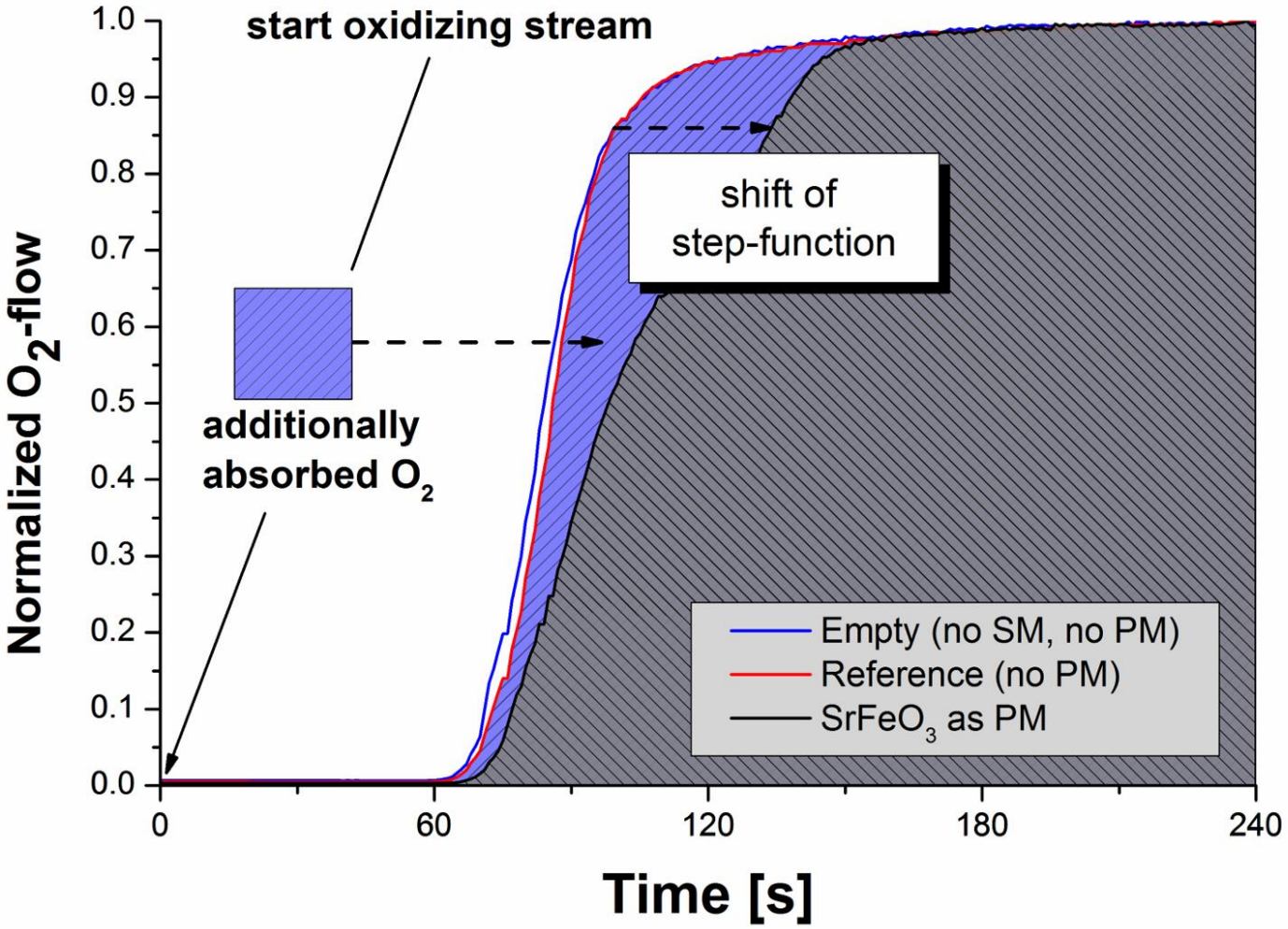
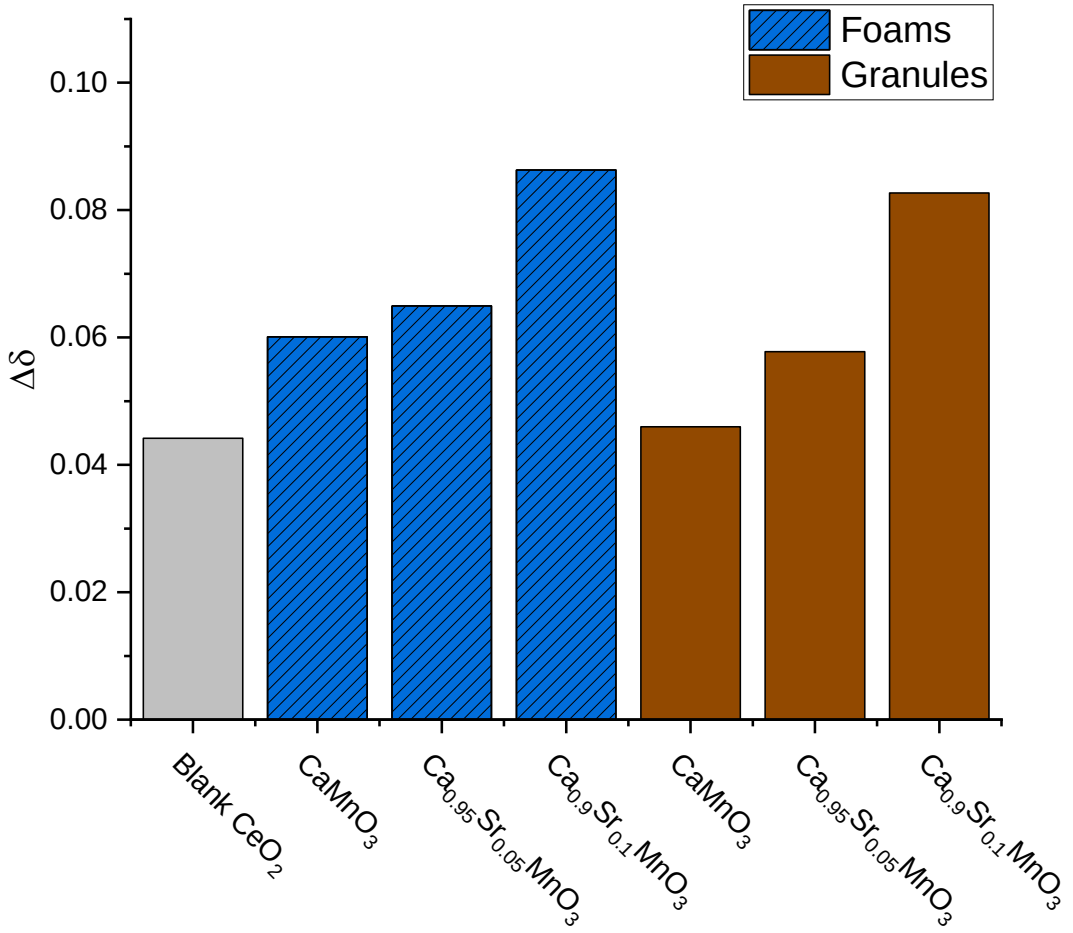
Experimental Principle



Pein et al., Solar Energy, Volume 198, 2020, Pages 612-622

Results - Oxygen Pumping with Foams and Granules

Seperate Temperature Swing



- Evacuated to 10^{-2} mbar
- Temperature swing applied
  - 1st: Pumping 800 °C – 700 °C
  - 2nd: Splitting 1500 °C – 1000 °C
  - Time for equilibration ~ 30 min
  - Pumping reactor disconnected

- Average increase of Δδ by 95% with $Ca_{0.9}Sr_{0.1}MnO_3$
- Foams and granules of $Ca_{0.9}Sr_{0.1}MnO_3$ perform equally good
- For $CaMnO_3$ trend towards foam

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Conclusions and Takeaways

- TCOP with Perovskites is a valid option to increase STCH efficiency
- Possible implementation of waste heat recovery
- $Ca_{1-x}Sr_xMnO_{3-\delta}$-Foams and Granules are suitable for TCOP applications
- Small amounts of A-site Sr-substitution beneficial for structure stability and TCOP performance

- Perovskites have high potential also for other thermochemical cyclic processes
- Fabrication of rigid, stable and efficient 3D-structures remains to be crucial
  - RPC, 3D-printing, Extrusion

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- Dr. Asmaa Eltayeb
- Dr. Martin Roeb
- Prof. Dr. Christian Sattler

<u>Relevant publications:</u>

- S. Brendelberger et al., Solar Energy, Volume 141, 2017, Pages 91-102
- M. Pein et al., Solar Energy, Vol. 198, 2020, 612-622
- M. Pein et al., *Adv. Energy Mater.* 2022, 12, 2102882
- *L. Klaas and M. Pein et al., Phys. Chem. Chem. Phys.*, 2022,24, 27976-27988

Thank you for your attention !

Questions ?

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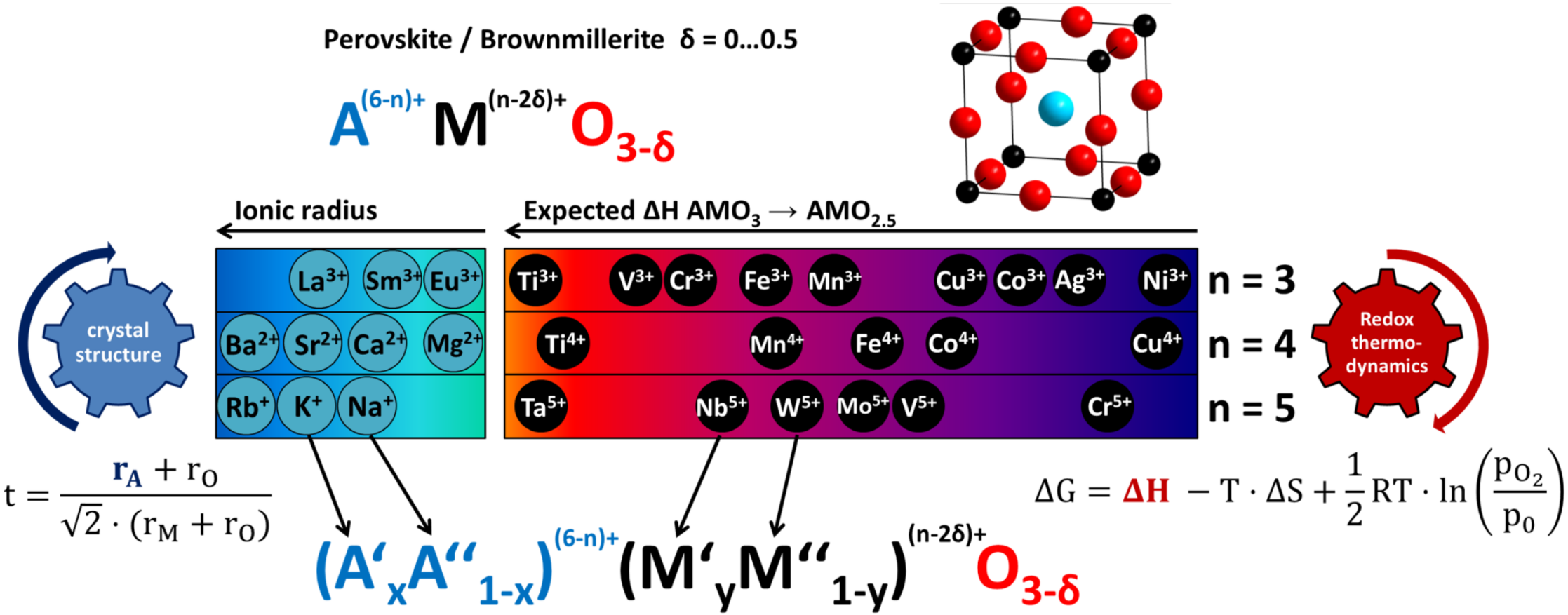
Perovskite Material Design



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2019. 12(4): p. 1369-1384