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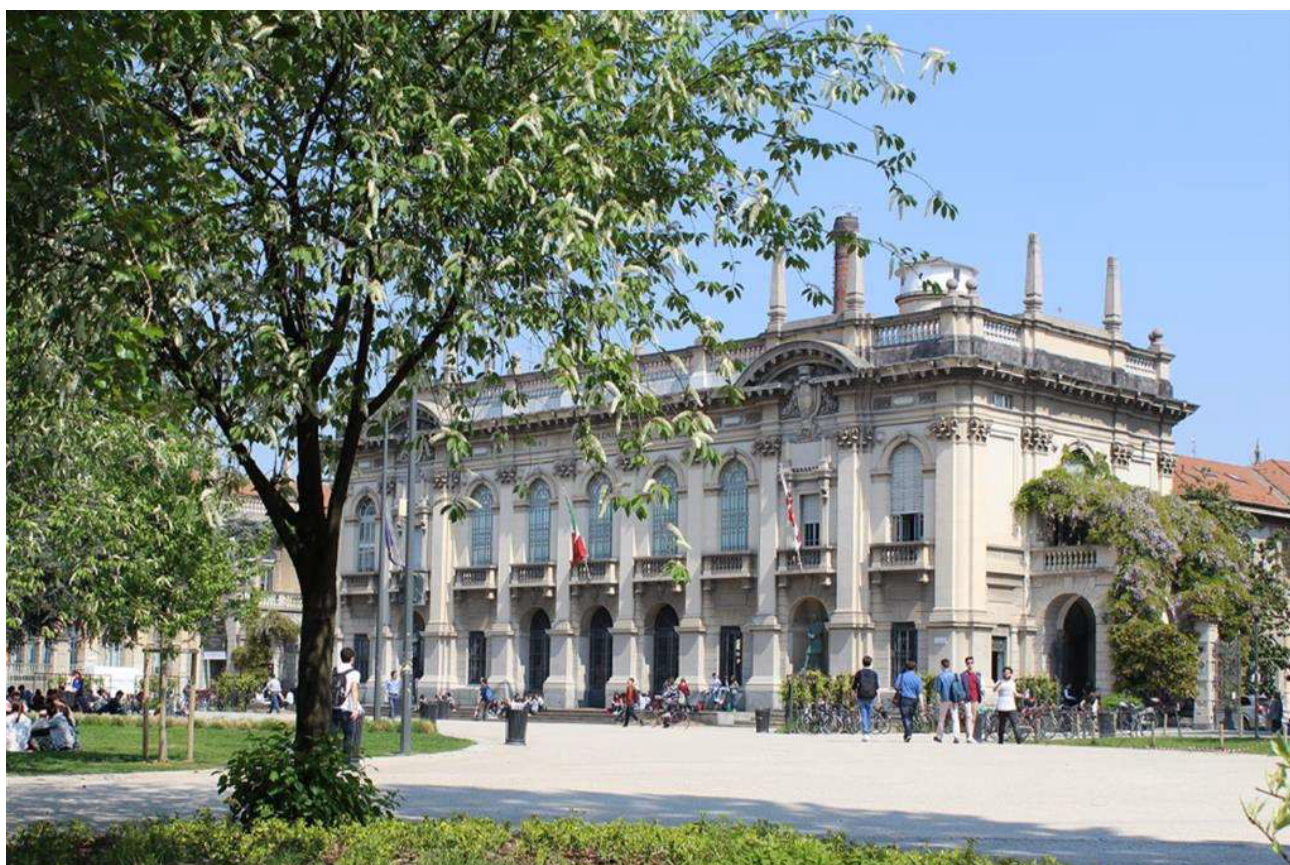


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XIII Congresso Nazionale AICIng e II Congresso Nazionale della Divisione di Chimica per le Tecnologie della SCI



ATTI DEL CONVEGNO

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Politecnico di Milano

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Doping Strategies for The Enhancement of The Thermochemical Heat Storage Capacity of CaMnO_3

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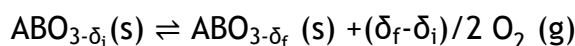
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Successful commercialization of concentrating solar power (CSP) plants requires effective energy storage for the supply of power on demand during solar transients. High temperature thermal energy storage (≥ 700 °C up to 1200 °C) has the potential to address not only the storage needs but also the power capacity due to the efficiency gains from high temperature operation. Perovskites (ABO_3) have been considered promising candidate for high temperature ThermoChemical heat storage (TCS) applications through oxygen exchange reactions [1]:



The amount of chemical heat stored per mole of material, or chemical heat storage capacity, is given as:

$$Q^M \left(\frac{\text{kJ}}{\text{kg}_{\text{ABO}_3}} \right) = \frac{1}{M_{\text{ABO}_3}} \int_{\delta_i}^{\delta_f} \Delta_{\text{red}} h \left(\frac{\text{kJ}}{\text{mol}_\text{O}} \right) d\delta$$

where $\Delta_{\text{red}} h$ is the enthalpy of reduction associated with the redox-reaction, δ_i is the initial oxygen non-stoichiometry (at $T = T_{\text{discharge}}$) and δ_f is the non-stoichiometry at a final condition of interest. Despite it is intuitive that the larger the reaction enthalpy ($\Delta_{\text{red}} h$) and extent ($\Delta\delta = \delta_f - \delta_i$) are, the larger would be the heat storage capacity. In reality, since the reaction enthalpy corresponds to the energy associated to the generation of oxygen vacancies, the higher is the reaction enthalpy (the more difficult is the material to be reduced/oxidized), the smaller is the reaction extent. Entropy is not a metric usually considered when estimating the thermochemical storage capacity of a material, but it is an essential property because the reaction extent depends monotonically on this term. Accordingly, materials with large entropy of reduction and intermediate enthalpy of reduction are desirable for chemical heat storage applications. We aim here at tuning the CaMnO_3 heat storage temperature window and

enhancing the heat storage properties by co-doping with equal amounts of La and Fe on the A and B sites, respectively $((La_xCa_{1-x})(Fe_xMn_{1-x})O_3)$. X-ray absorption spectroscopy and diffraction studies revealed that Fe and Mn adopt, respectively, the 3+ and 4+ oxidation states under ambient conditions, and that the dopants are incorporated into the intended octahedral B sites. Interestingly, the chemical heat storage capacity depends on both reaction enthalpy and reaction extent, and the $La_{0.05}Ca_{0.95}Fe_{0.05}Mn_{0.95}O_{3-\delta}$ composition offers a more attractive combination of these factors than the 10% La doped composition, despite a lower reaction enthalpy in the former. This result is a consequence of the substantially larger extent of reduction enabled by the higher entropy than that of $La_{0.1}Ca_{0.9}Fe_{0.1}Mn_{0.9}O_3$. Under technologically relevant conditions, operating over a temperature window of 700 to 1200 °C and under an oxygen partial pressure of about 10^{-3} atm, the thermochemical heat storage capacities of $La_{0.05}Ca_{0.95}Fe_{0.05}Mn_{0.95}O_3$ and $La_{0.1}Ca_{0.9}Fe_{0.1}Mn_{0.9}O_3$ are 378.5 ± 1.0 kJ/kg_{ABO₃} and 282.3 ± 1.5 kJ/kg_{ABO₃}, respectively, and exceed the values not only of the undoped material, but for the first material also of different singly doped analogs (Figure 1) [2,3]. Furthermore, with respect to the singly Fe-doped CaMnO₃ we narrowed the operating temperature range from 400-1200 °C to 700-1200 °C, that is the target one for the CSP plants. Hence, we demonstrated that by co-doping it is possible to tailor reduction enthalpy and extent, together with the operating temperature range.

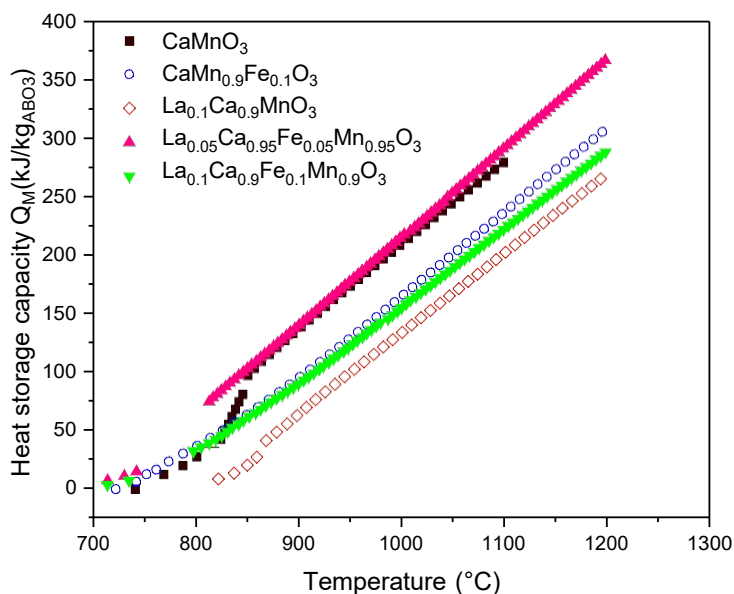


Figure 1. Comparison $La_{0.05}Ca_{0.95}Fe_{0.05}Mn_{0.95}O_3$ and $La_{0.1}Ca_{0.9}Fe_{0.1}Mn_{0.9}O_3$ with previously investigated compositions CM, CMF10 and LCM10 under similar operating conditions ($p_{O_2}=10^{-3}$ atm, $T_{dis}=700$ °C, $T_{ch}=1200$ °C).

References

- [1] S. M. Babiniec, E. N. Coker, J. E. Miller and A. Ambrosini, *Int J Energy Res*, **2015**, 6-10.
- [2] E. Mastronardo, X. Qian, J. M. Coronado and S. M. Haile, *J Mater Chem A Mater*, **2020**, *8*, 8503-8517.
- [3] E. Mastronardo, X. Qian, J. M. Coronado and S. M. Haile, *J Energy Storage*, **2021**, *40*, 102793.