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TITLE: **Efficient perovskite-based high-temperature hybrid sensible-thermochemical heat storage systems for integration with renewable energy sources**

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Abstract
The present work presents a holistic approach on development of efficient high-temperature heat storage systems for integration with renewable energy (RE) sources as well as industrial waste heat recovery. The concept pursued is that of hybrid sensible-thermochemical storage implemented on porous, flow-through ceramic monolithic structures like honeycombs and foams, manufactured entirely or substantially from earth-abundant, inexpensive, environmentally-benign perovskites. Ca-Mn-based perovskites in particular, are capable of cyclic, reversible reduction-oxidation (redox) under air atmosphere, accompanied by significant endothermal/ exothermal heat effects, according to the scheme: $\mathrm{CaM}n\mathrm{O}_3 \leftrightarrow CaMn\mathrm{O}_{3-\delta} + \frac{\delta}{2}\mathrm{O}_2$. The necessary "renewable" heat for the endothermic reduction step can be supplied from, otherwise to-be-curtailed, surplus electricity from PV or wind systems, concentrated solar energy or hot industrial waste gas streams. This heat is recovered by the inverse, exothermic oxidation of the reduced oxide when the RE-source is not available. With redox oxides, air can be used as both the heat transfer fluid and the reactant (O_2) coming into direct contact with the storage material (oxide).
The development of $CaMnO_3$-based redox structures is addressed starting from high-throughput computational screening of such A- and B-site doped perovskite compositions to extract via Density Functional Theory (DFT) theoretical key metrics like heat capacity (extremely important for sensible heat storage), redox reactions enthalpy and thermo-mechanical properties within the temperature range of interest, as a function of kind and concentration of dopant elements. The so-identified shortlisted multi-cation perovskite compositions are synthesized by scalable routes, optimizing selection of precursor powders and sintering conditions with respect to the targeted properties of merit like phase purity of the obtained perovskite, heat capacity, extend and reversibility of reduction, heat effects of the redox reactions, coefficient of thermal expansion, and dimensional changes due to thermochemical expansion/contraction, among others. Of significant importance is the absence of phase transformations, which, even though reversible during heating/cooling in the temperature range of 300-1100°C, are nevertheless detrimental on the thermomechanical strength and longevity of structured ceramics. Finally, rigid monolithic porous honeycombs and foams were manufactured from such optimized compositions in a variety of sizes spanning from few mm to tens of cm. Long-term cyclic redox tests (>200 cycles) on such structures have demonstrated for the first time the ability of a perovskite – or in general of a redox oxide operating via partial reduction (oxygen vacancies) mechanism - to generate repeatable heat effects manifested as sensible temperature rise of a working/heat transfer fluid upon cyclic redox operation.