Assessment of the Gibbs energies of Perovskites in the system Ca-Mn-Sr-O using the Calphad Optimizer (CO)

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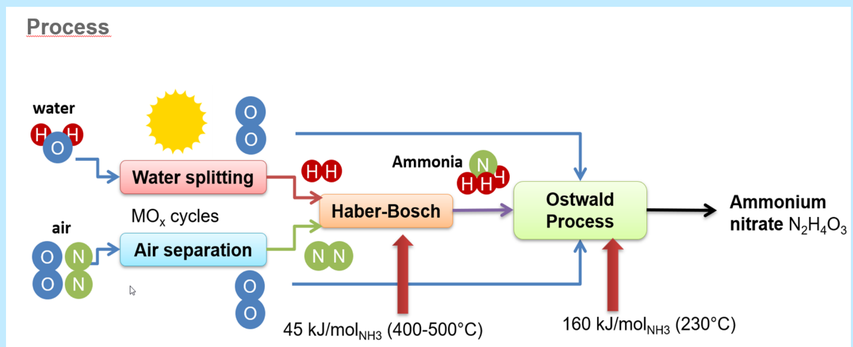
1. Background

Using solar energy for the production of fertilizer (N2H4O3) on the basis of water and air provides a promising route in terms of green industry. The figure below shows the production route. In this, the air separation plays an important role. In order to extract the oxygen a storage medium is needed which can be loaded and unloaded in a temperature cycle.



Process route for the production of ammonium nitrate from water and air using solar power

The Perovskites $CaMnO_{3-\delta}$ and $(Ca,Sr)MnO_{3-\delta}$ show continuous non-stoichiometry for oxygen over a wide range of temperatures and oxygen partial pressures. They are therefore of particular interest to industry, as they can be used as such a storage medium. Despite their importance, the phase equilibria in these systems have not yet been well investigated. The experimental investigation of the entire system is complicated because of the strong dependence of the equilibria on the oxygen partial pressure and the high melting temperature of the solid phases. Therefore, a critical evaluation of the data is required to better understand and model these systems.

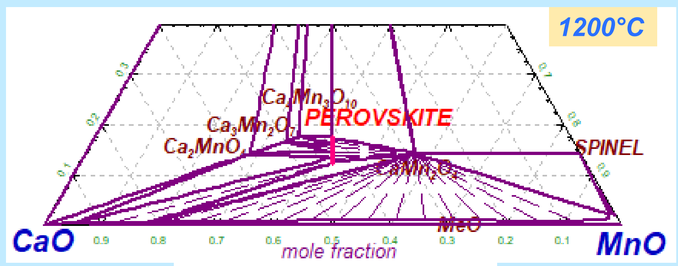
References

[Klaas 2021] L. Klaas, D. Guban, M. Roeb, C. Sattler. (2021) Recent Progress towards solar energy integration into low-pressure green ammonia production technologies, *International Journal of Hydrogen Energy*.

[Bulfin2017] B. Bulfin, J. Vieten, D.E. Starr, A. Azarpira, et al., J. Materials Chemistry A, (2017), 5, 7912-7919.

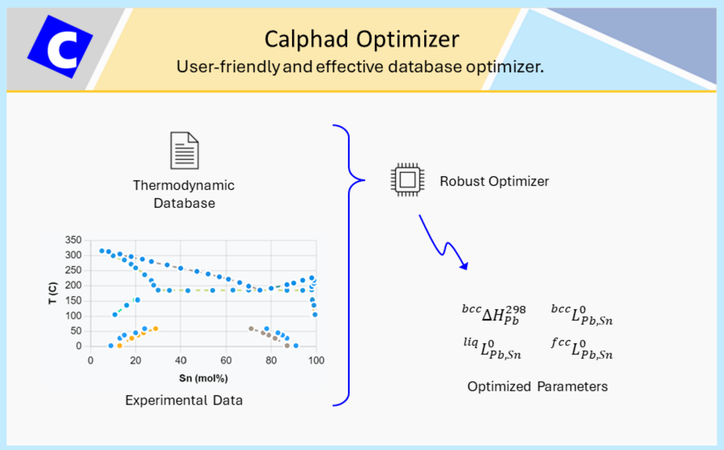
2. Perovskite $CaMnO_{(3-\delta)}$

Metal oxides with multivalent species are very valuable for applications as redox materials. The occurrence of an oxygen non-stoichiometry δ (δ = 0-0.5) in $AMO_{3-\delta}$ perovskites and the close structural relationship between perovskites and their reduced form $A_2M_2O_5$ (brownmillerite) in a defect arrangement reveals fast redox kinetics, which depend on partial pressure of oxygen and temperature:



$$AMO_3 \xleftrightarrow{T,pO_2} AMO_{3-\delta} + \frac{\delta}{2}O_2,$$

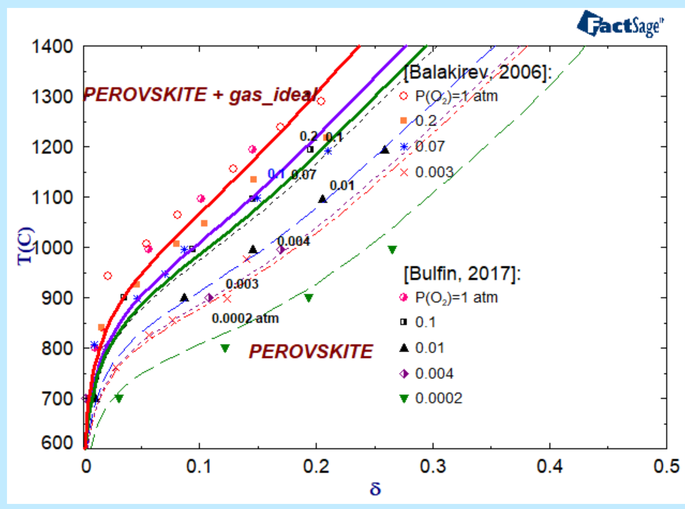
3. CALPHAD optimizer



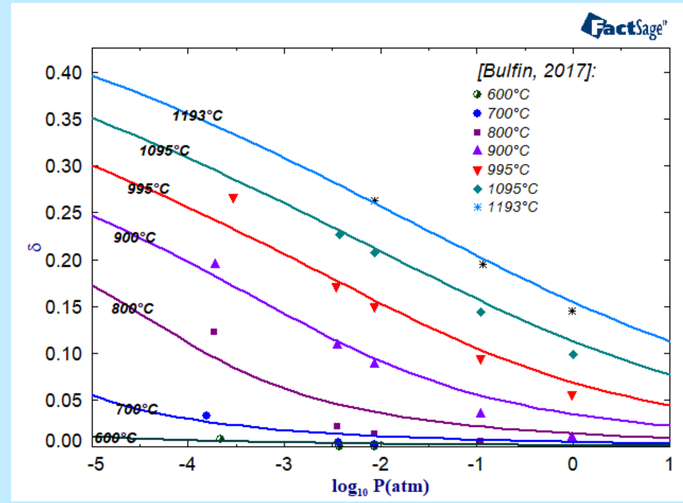
References

[Calphad Optimizer] Calphad Optimizer Module Archives - GTT-Technologies, GTT-Technologies, (2024), https://gtt-technologies.de/category/factsage/calphad-optimizer

4. Data Assessment



Temperature dependence of oxygen nonstoichiometry (δ) in $CaMnO_{(3-\delta)}$ for various partial pressures of oxygen.



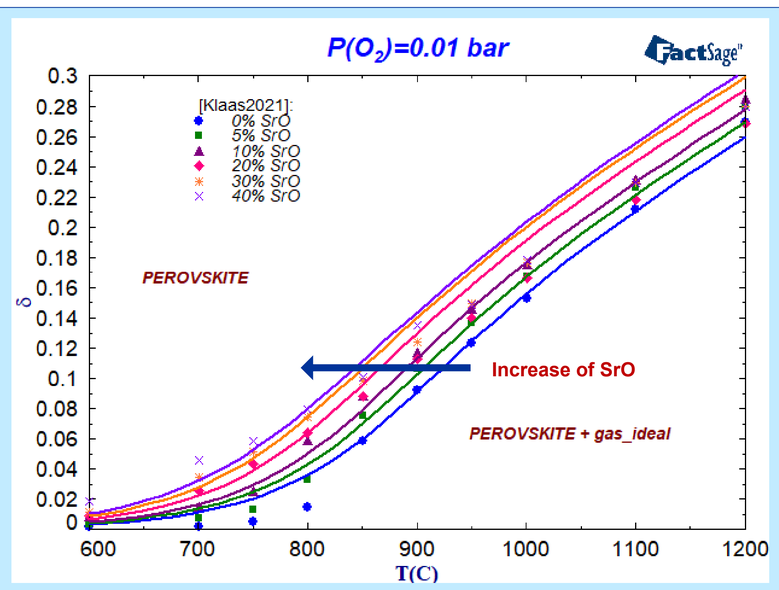
Measured and calculated oxygen nonstoichiometry (δ) of $CaMnO_{(3-\delta)}$ as function of O_2-partial pressure for various constant temperatures.

5. Influence of strontium enrichment on the properties of Perovskite

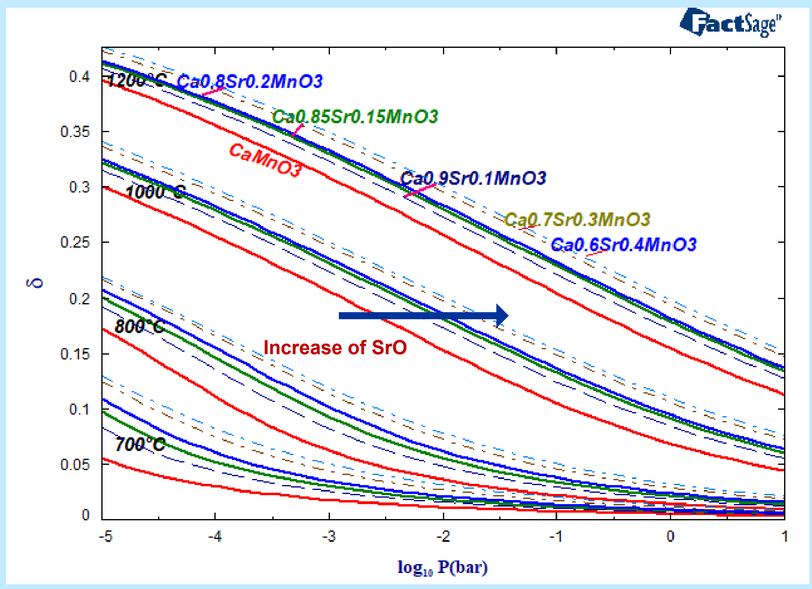
L. Klaas and D. Guban [Klaas2021] measured the equilibrium non-stoichiometry of the materials $CaMnO_3$,$Ca_{0.9}Sr_{0.1}MnO_3$,$Ca_{0.85}Sr_{0.15}MnO_3$, $Ca_{0.8}Sr_{0.2}MnO_3$, $Ca_{0.7}Sr_{0.3}MnO_3$, $Ca_{0.6}Sr_{0.4}MnO_3$ in the temperature range from 400 to 1200°C and at oxygen partial pressures of 1 to 10^{-5} bar using a thermobalance and oxygen pump.

The thermodynamic database Ca-Mn-O was augemented by Sr. Perovskite was modelled as **$(\underline{Ca^{+2}}, Sr^{+2})(Mn^{+3},\underline{Mn^{+4}})(\underline{O^{-2}},Va)_3$** where the major constituents are underlined.

The experimental data [Bulfin2017], [Klaas2021] were used to extend the thermodynamic data of the Perovskite so that meaningful process simulations could also be carried out for higher strontium concentrations.



Temperature dependence of oxygen nonstoichiometry (δ) of $(Ca_{1-x}Sr_x)MnO_{(3-\delta)}$ for various constant amount of SrO at $P(O_2)$=0.01 atm.



Measured and calculated oxygen nonstoichiometry (δ) of $(Ca,Sr)MnO_{(3-\delta)}$ as function of O_2-partial pressure for various constant temperatures.

6. Conclusions

For lower temperatures and higher O_2-partial pressures, the perovskites with higher proportions of SrO (e.g. $Ca_{0.7}Sr_{0.3}MnO_3$ and $Ca_{0.6}Sr_{0.4}MnO_3$) exhibit a greater extent of reduction δ than $CaMnO_3$. However, these perovskites decompose at lower temperatures and higher partial pressures as compared to pure $CaMnO_3$.

The use of this database enables calculations in the quaternary system Ca-Mn-Sr-O and predictions of oxygen partial pressures at different temperatures and composition ranges of the perovskites. The general agreement between the calculated phase equilibria as well as the thermodynamic properties and the respective experimental data is good.

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