Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information: Redox chemistry of $CaMnO_3$ and $Ca_{0.8}Sr_{0.2}MnO_3$ oxygen storage perovskites

Sample preperation

For the preparation of $CaMnO_3$, 50 mL of a 0.1 M aqueous solution of calcium nitrate tetrahydrate (99 %, Alfa Aeasar) were mixed with 50 mL of a 0.1 M manganese(II)-nitrate tetrahydrate solution (for analysis, Acros Organics) and 4 mL of a 5 M citric acid solution (99 %, Merck).

$Ca_{0.8}Sr_{0.2}MnO_3$ was prepared by mixing 40 mL of the 0.1 M $Ca(NO_3)_2$ solution with 50 mL of 0.1 M $Mn(NO_3)_2$ solution and 4 mL of a 5 M citric acid solution. The mixture was heated to boiling point and 0.148 g of strontium carbonate (99.99 %, Alfa Aeasar, 1.0 mmol) were added, which dissolved readily under the formation of CO_2 gas.

The water from the resulting mixtures was removed by evaporation, leading to the formation of a viscous gel. The temperature was elevated from 130 to 200 °C in steps of 10 °C within 15 min, leading to the decomposition of citrate ions. Subsequently, the dried gels were heated to 300 - 500 °C, and the resulting auto-combustion lead to the formation of finely dispersed oxide powders. These were then calcined twice at 800 °C for 10 h and once at 1300 °C for 20 h.

TGA raw data

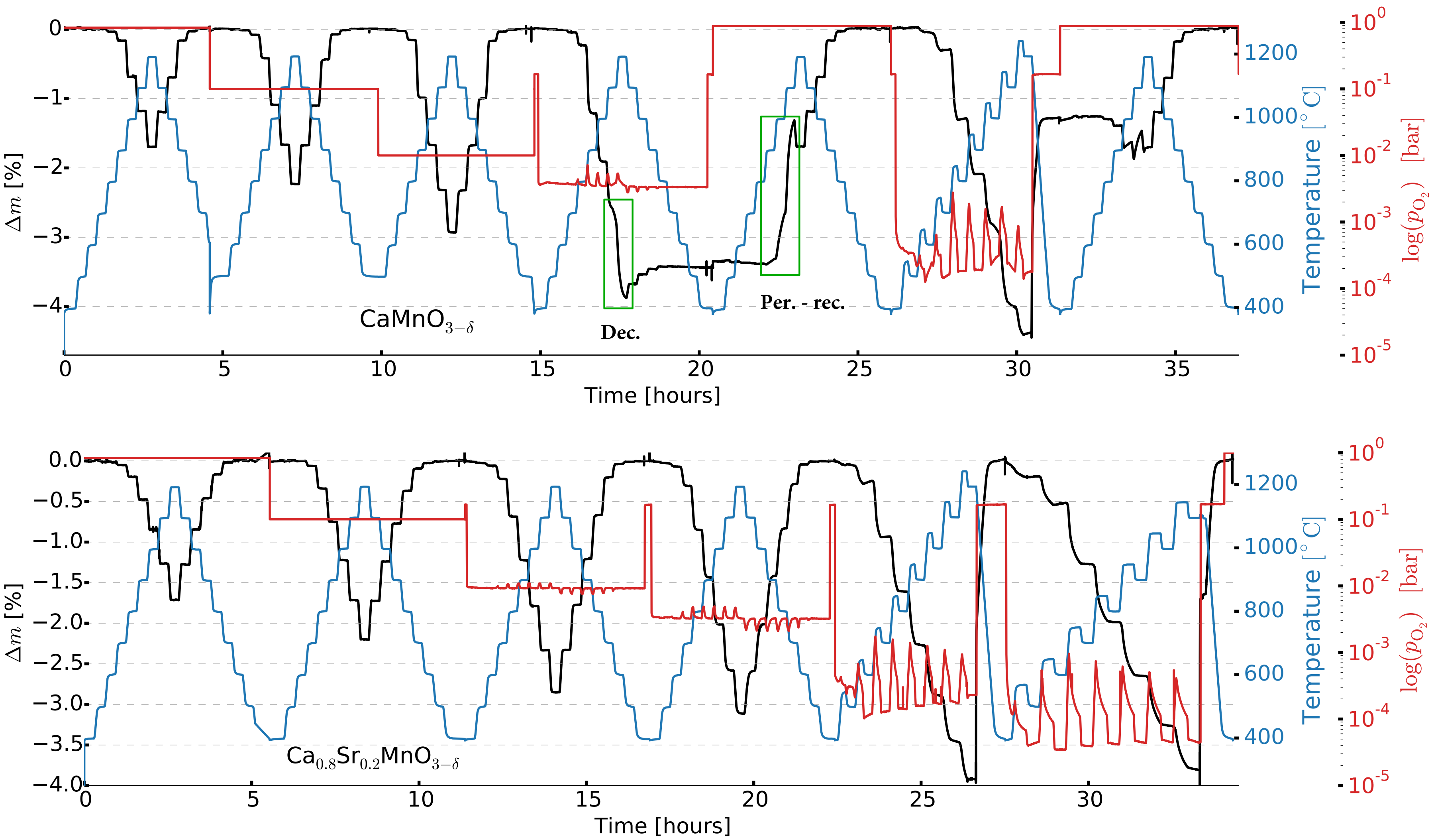


Figure 1: The full TGA data sets used for each material with the mass change plotted in black to the left axis and the temperature and partial pressure plotted to the right to their respective colored axis. At low partial pressures the temperature was first increased to remove oxgen faster and then cooled again, which allows the system to attain equilibrium more rapidly. **Above:** CaMnO$_3$ data with an observed decomposition marked with the green rectangle labelled Dec. and the recovery of the perovskite under high p_{O_2} and T marked Per. rec.. **Below:** Ca$_{0.8}$Sr$_{0.2}$MnO$_3$ data.

XRD and EDX

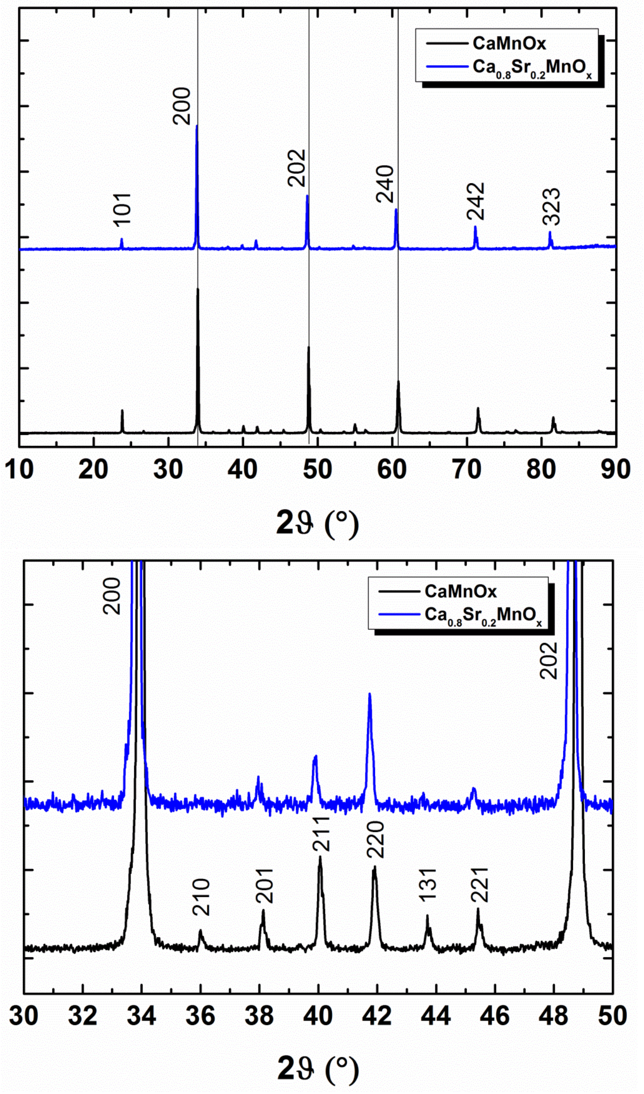


Figure 2: X-Ray diffractograms of $Ca_{0.8}Sr_{0.2}MO_3$ and $CaMnO_3$ with indexed peaks. **Above:** The shift of reflections towards lower 2θ values indicates the lattice expansion due to the incorporation of Sr into the lattice. **Below:** The decreasing intensity of small reflections in the Sr doped sample might indicate a lower distortion of the ideal cubic structure.

Table 1: Refined cell parameters and structure of pure CaMnO$_3$ and Ca$_{0.8}$Sr$_{0.2}$MO$_3$.

	CaMnO$_3$	Ca$_{0.8}$Sr$_{0.2}$MnO$_3$
Refined space group	Pnma (62), orthorhombic	Pnma (62), orthorhombic
Cell paramaters		
a	5.278 ± 0.002 Å	5.298 ± 0.002 Å
b	7.463 ± 0.002 Å	7.493 ± 0.002 Å
c	5.277 ± 0.002 Å	5.298 ± 0.002 Å

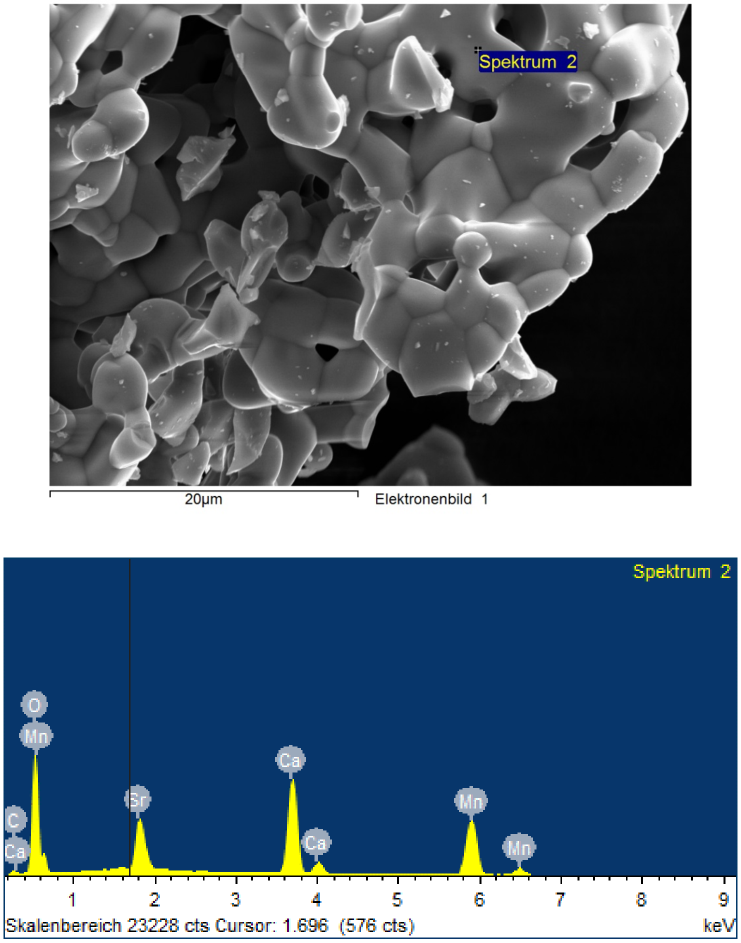


Figure 3: Three different EDX spectra were taken at different areas of the Ca$_{0.8}$Sr$_{0.2}$MnO$_3$ sample. Taking an average of the atomic percentages from each scan indicated the composition Ca$_{0.78}$Sr$_{0.22}$MnO$_3$ which confirmed the composition within the error of the measurements.

$CaMnO_3$ Decomposition

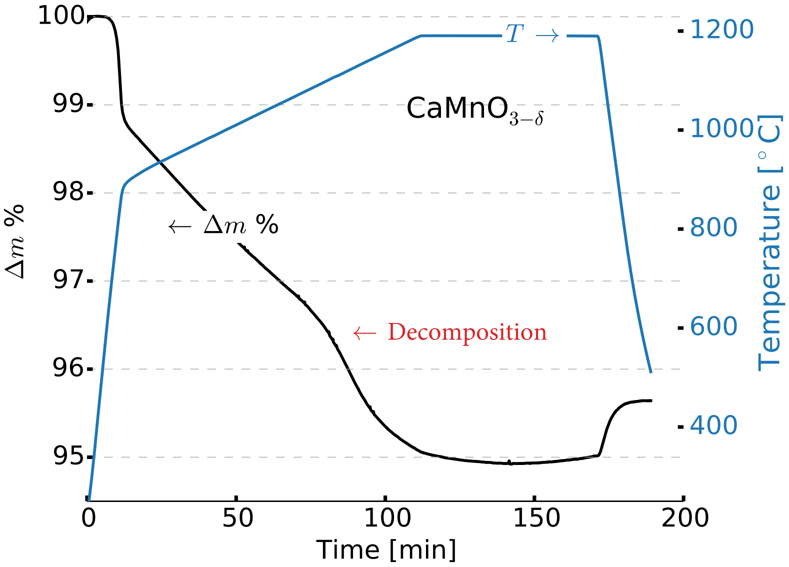


Figure 4: A TGA scan of $CaMnO_3$ in an argon atmosphere mixed with synthetic air. The oxygen partial pressure was $p_{O_2} = 0.004$ bar. The approximate position where the perovskite begins to decompose is marked.

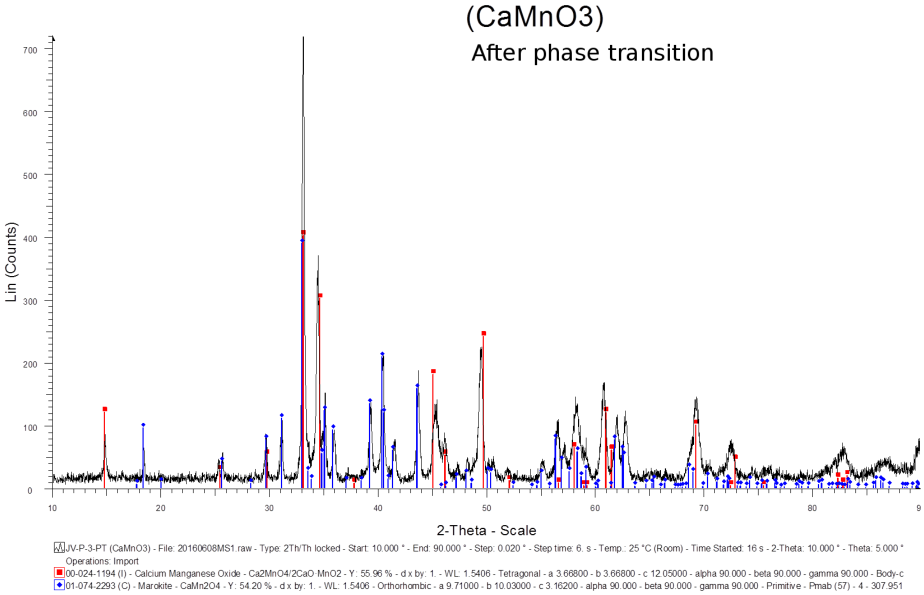


Figure 5: XRD after the decomposition. The perovskite is lost and the XRD pattern shows a mixture of calcium manganese oxide $Ca_2MnO_4/2CaOMnO_2$ and marokite $CaMn_2O_4$.

X-ray Spectroscopy

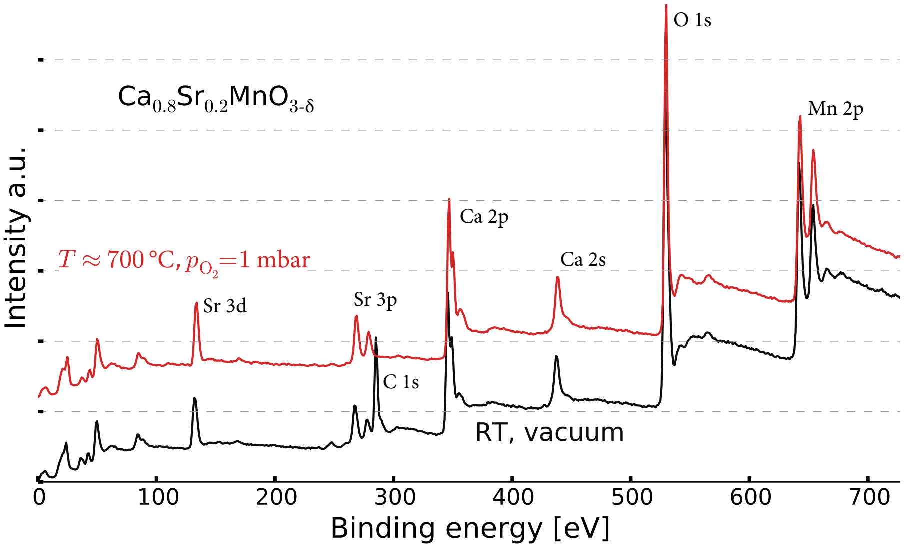
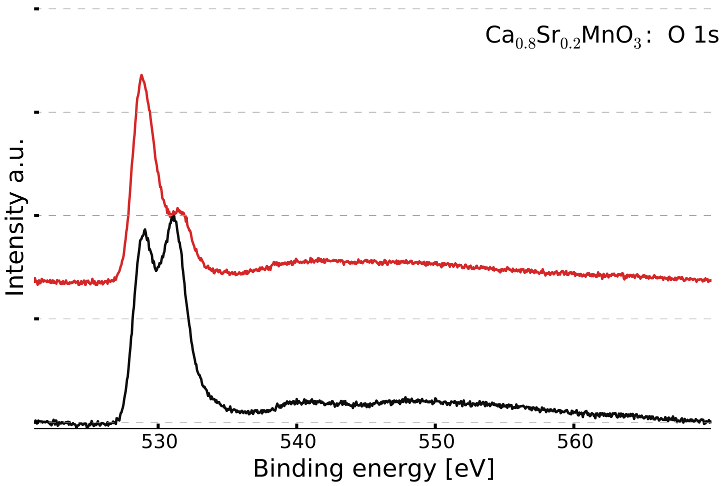
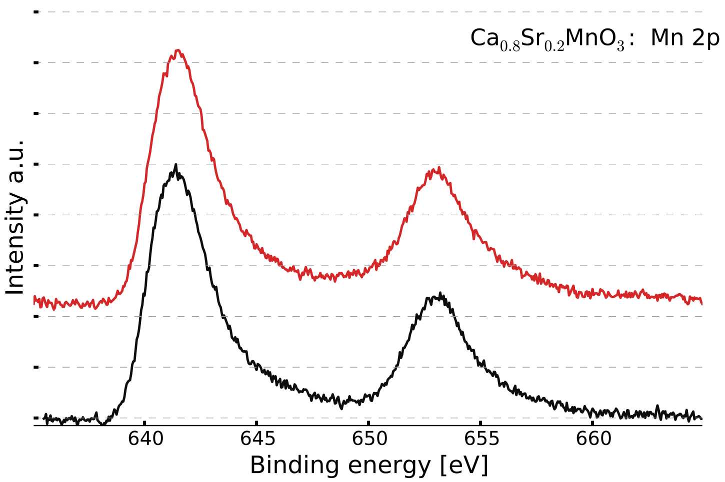
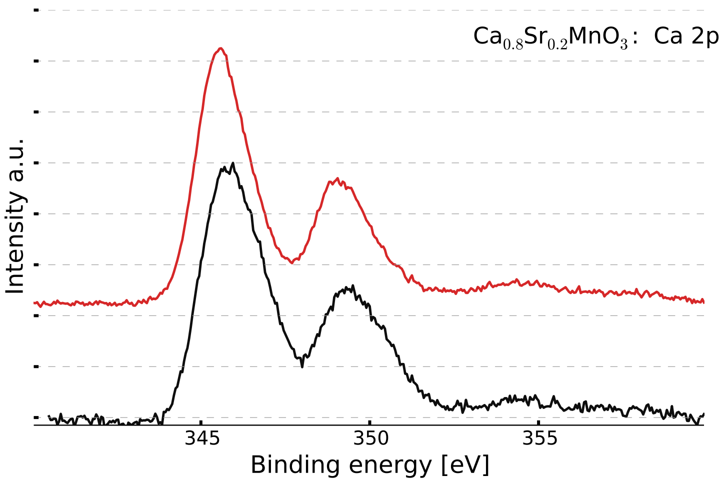
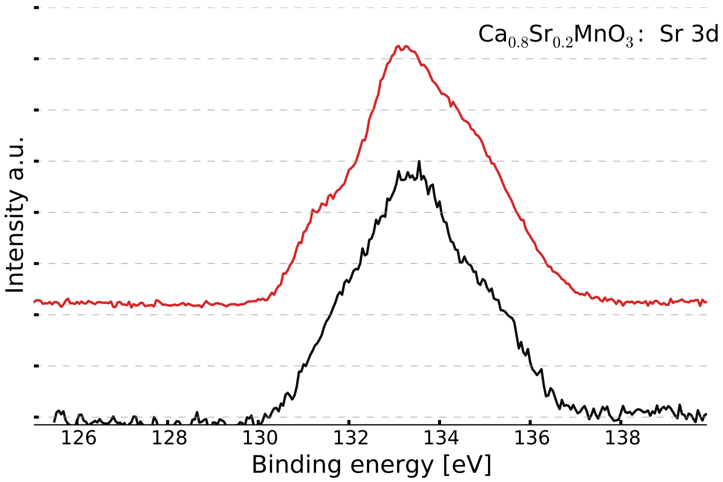


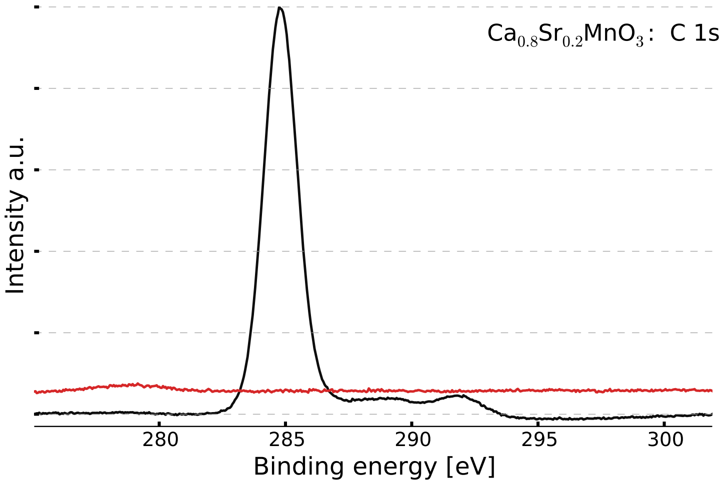
Figure 6: XPS of the $Ca_{0.8}Sr_{0.2}MO_3$ sample, as loaded at room temperature under high vacuum conditions, and at 700 ° C and 1 mbar oxygen partial pressure. Below is a look at the most prominent peaks of each species, under the same conditions and using the same colors. Also shown is the C 1s peak which disappears after heating in an oxygen atmosphere.




$Ca_{0.8}Sr_{0.2}MnO_3$: Mn 2p
Intensity a.u.
640
645
650
655
660
Binding energy [eV]


$Ca_{0.8}Sr_{0.2}MnO_3$: Ca 2p
Intensity a.u.
345
350
355
Binding energy [eV]


Ca$_{0.8}$Sr$_{0.2}$MnO$_3$: Sr 3d
Intensity a.u.
126
128
130
132
134
136
138
Binding energy [eV]


Ca$_{0.8}$Sr$_{0.2}$MnO$_3$: C 1s
Intensity a.u.
280
285
290
295
300
Binding energy [eV]