SUPPORTING INFORMATION

High redox activity of Sr-substituted lanthanum manganite perovskites for two-step thermochemical dissociation of CO_2

Antoine DEMONT, Stéphane ABANADES[*]

Processes, Materials, and Solar Energy Laboratory, PROMES-CNRS (UPR 8521), 7 Rue du Four Solaire, 66120 Font-Romeu, France

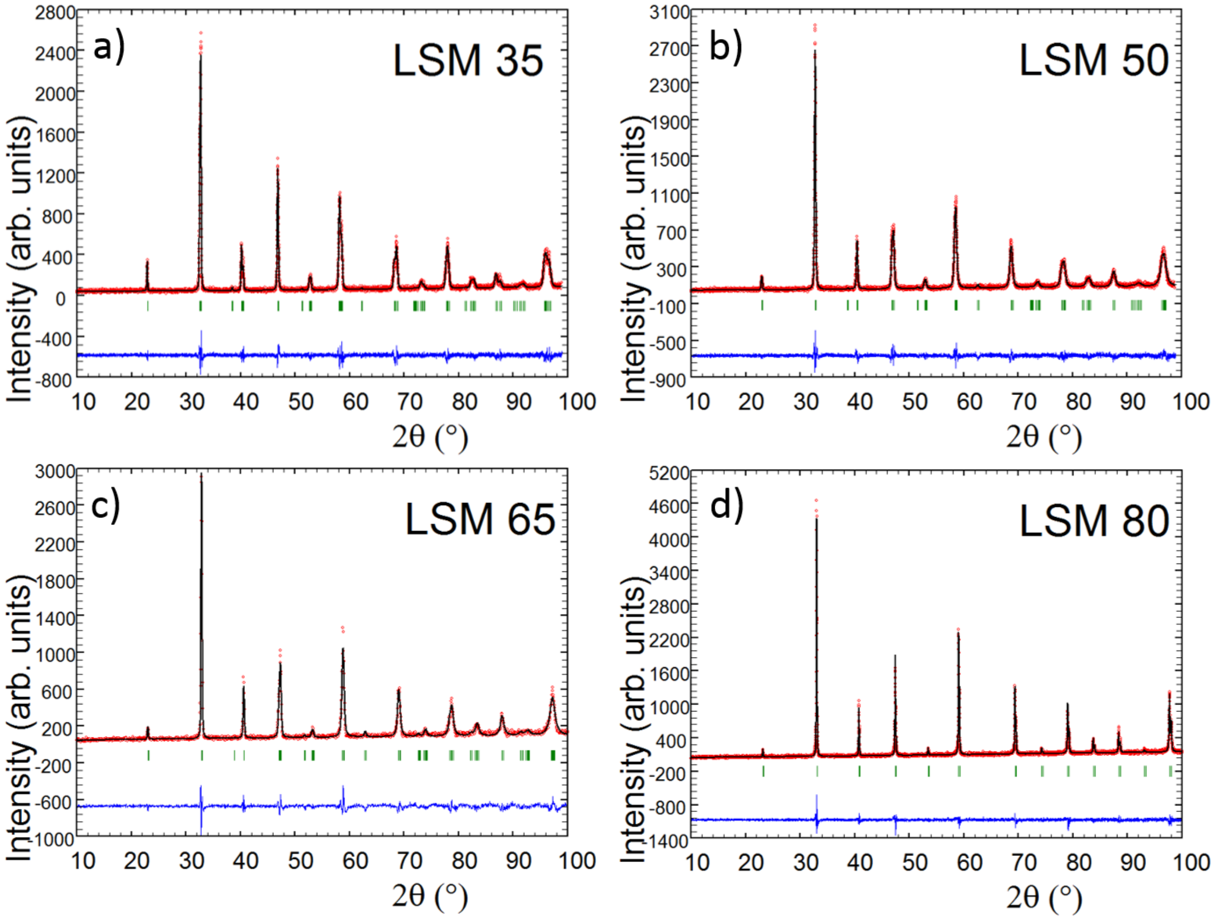

Figure SI1: LeBail fits of powder X-ray diffraction data collected on LSM perovskites. Experimental (red), calculated (black) and difference (blue) curves are shown.

Phase identification was performed with powder X-ray diffraction (PXRD), showing that all samples were single phase perovskites. In order to verify for strontium introduction in the $LaMnO_3$ based perovskites, LeBail fits were performed, enabling to point out the evolution of crystal symmetries and cell parameters within the series (Figure SI1). Distortions of the crystal lattice are observed for LSM35 ($R\,\overline{3}c$), LSM50 ($I\,4/mcm$), and LSM65 ($I\,4/mcm$), producing perovskites superstructures of different orders. No splitting of the reflections was observed in the case of LSM80, and the $P\,m\overline{3}m$ symmetry was used to calculate the model. Table SI1 summarizes the results gathered from these LeBail fits.

	Goldschmidt tolerance factor	Space group	Cell parameters relationship	a (Å) ***a_p (Å)***	b (Å) ***a_p (Å)***	c (Å) ***a_p (Å)***	V (Å^3) ***a_p^3 (Å^3)***
LSM 35	0.990	$R\bar{3}c$	$a = a_p\sqrt{2}$ $b = a_p\sqrt{2}$ $c = 2a_p\sqrt{3}$ $V = \sin 120 \times 4a_p^3 \times \sqrt{3}$	5.49772(7) ***3.88747(5)***	5.49772(7) ***3.88747(5)***	13.3609(3) ***3.8570(1)***	349.729(8) ***58.289(2)***
LSM 50	1.001	$I\,4/mcm$	$a = a_p\sqrt{2}$ $b = a_p\sqrt{2}$ $c = 2a_p$ $V = 4a_p^3$	5.4479(2) ***3.8522(2)***	5.4479(2) ***3.8522(2)***	7.7494(2) ***3.8747(1)***	229.995(8) ***57.499(2)***
LSM 65	1.017	$I\,4/mcm$	$a = a_p\sqrt{2}$ $b = a_p\sqrt{2}$ $c = 2a_p$ $V = 4a_p^3$	5.4278(3) ***3.8381(3)***	5.4278(3) ***3.8381(3)***	7.7147(6) ***3.8573(4)***	227.29(3) ***56.822(1)***
LSM 80	1.031	$P\,m\bar{3}m$	$a = a_p$ $b = a_p$ $c = a_p$ $V = a_p^3$	3.82726(2) ***3.82726(2)***	3.82726(2) ***3.82726(2)***	3.82726(2) ***3.82726(2)***	56.061(1) ***56.061(1)***

Table SI1: Goldschmidt tolerance factor calculated from data tabulated by R.D. Shannon[1] and summary of the structural characteristics of the LSM compounds determined from LeBail fits. The cell parameter relationship column refers to the relation of the perovskite superstructure to the ideal cubic perovskite structure. a_p refers to the cell parameter of a simple cubic perovskite structure.

Calculated Goldschmidt tolerance factors show a monotonic evolution along the LSM series and account for the crystal symmetry evolution observed within the series. The increase of this ratio with Sr content moderates the distortion that is initially present in non-substituted $LaMnO_3$ and eventually leads to a cubic symmetry in the case of LSM80. Due to superstructures of different order, the metrics of the unit cells are not directly comparable within the series. For example, the volume of the unit cell corresponds to 4 formula units (f.u.) in the case of LSM50, whereas it only corresponds to 1 f.u. in the case of LSM80. A more direct comparison is allowed by establishing the crystallographic relationships between these superstructures and the simple cubic perovskite. Thus, the a_p^3 value quoted in Table SI1 represents the volume (V) per f.u. for each compound, and it is a quantity that is directly comparable throughout the series.

Throughout the LSM series, the clear decrease in V per f.u. confirms the Sr introduction in these $LaMnO_3$ based perovskites. One should note that Sr^{2+} has a larger ionic radius than La^{3+} (1.44 Å versus 1.36 Å). However, the substitution of La^{3+} cations by Sr^{2+} cations is accompanied by the substitution of Mn^{3+} by Mn^{4+}. The large size difference between Mn^{3+} (0.645 Å) and Mn^{4+} (0.53 Å) accounts for the aforementioned decrease of the V per f.u., which is also evidenced by the shift of diffraction peaks toward higher angles as the Sr^{2+} content increases. In summary, the compounds synthesized here could clearly be identified on the basis of PXRD, owing to their peak positions, crystal symmetries and cell parameter evolution with Sr^{2+} substitution for La^{3+}.

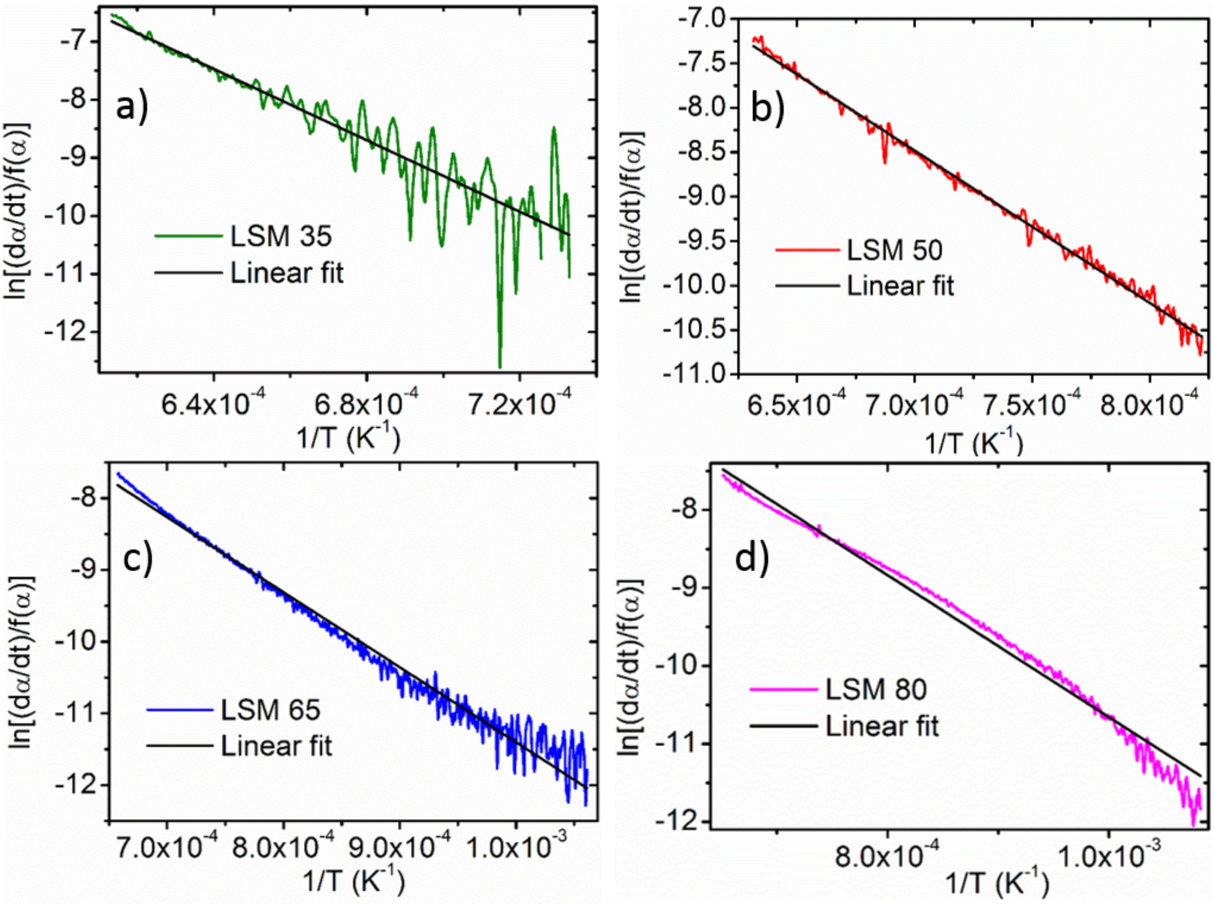

Figure SI2: Linear fits used to determine the activation energies for the reduction of LSM35, LSM50, LSM65 and LSM80.

In order to determine the activation energies, the contracting sphere model was applied. The conversion fraction α was determined as follows:

$\alpha = (m_0 - m_t)/(m_0 - m_f)$

where m_0 is the mass before the reduction, m_t is the mass at time t and m_f is the final mass at the end of the reduction step.

According to the contracting sphere model, the reaction model was calculated as:

$f(\alpha) = 3(1 - \alpha)^{2/3}$

The rate of a solid-state reaction can generally be described as:

$d\alpha/dt = Ae^{-(Ea/RT)}f(\alpha)$

where A is the pre-exponential factor (constant, s^{-1}), E_a is the activation energy (J/mol), T is the absolute temperature and R is the gas constant.

Therefore:

$\ln[(d\alpha/dt)/f(\alpha)] = A - (E_a/R)(1/T)$

and the plot of $\ln[(d\alpha/dt)/f(\alpha)] = f(1/T)$ (Figure SI2) gives access to E_a.

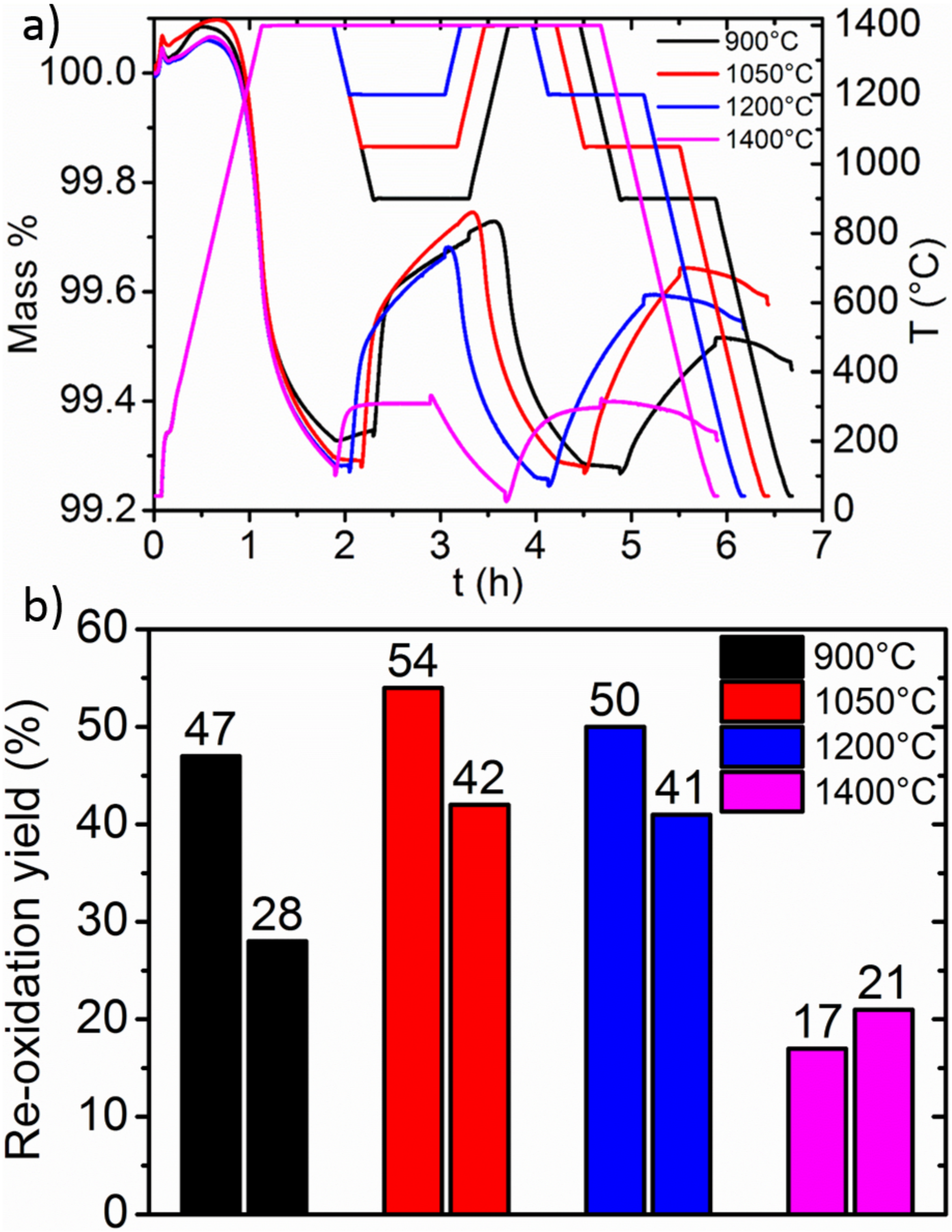

Figure SI3: a) TG curves collected for LSM50 during reduction at 1400°C under Ar followed by exposure to CO_2 at different temperatures (two cycles). b) Re-oxidation yields associated to the different temperatures of re-oxidation.

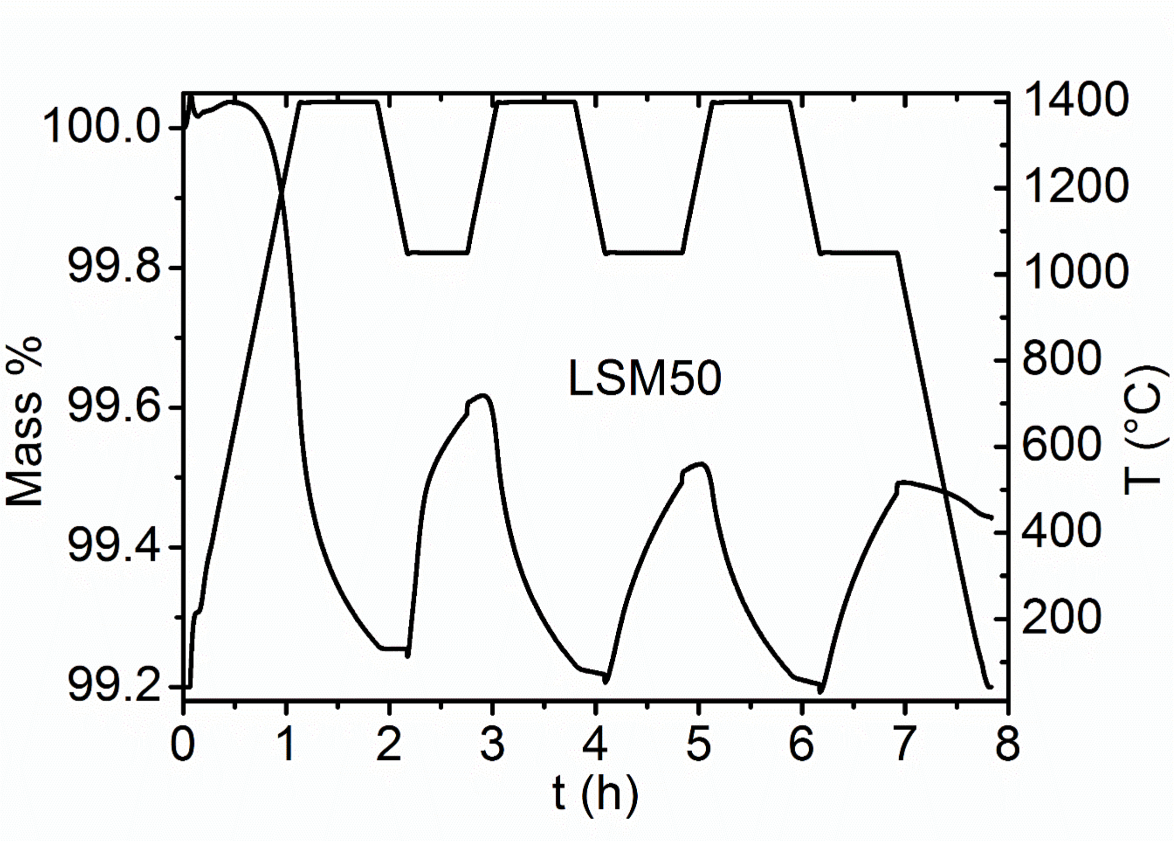

Figure SI4: TG curve collected for LSM50 during reduction at 1400°C under Ar followed by exposure to CO_2 at 1050°C (three cycles).

Reference

1. R.D. Shannon, *Acta Cryst.* **A32** 751-767 (1976)