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## Reversible Phase Transformations in Novel Ce-Substituted Perovskite Oxide Composites for Solar Thermochemical Redox Splitting of CO<sub>2</sub>

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Thermochemical splitting of CO<sub>2</sub> and H<sub>2</sub>O via two-step metal oxide redox cycles offers a promising approach to produce solar fuels. Perovskitetype oxides with the general formula ABO<sub>3</sub> have recently gained attention as an attractive redox material alternative to the state-of-the-art ceria, due to their high structural and thermodynamic tunability. A novel Cesubstituted lanthanum strontium manganite perovskite-oxide composite, La<sup>3+</sup>0.48Sr<sup>2+</sup>0.52(Ce<sup>4+</sup>0.06Mn<sup>3+</sup>0.79)O<sub>2.55</sub> (LSC25M75) is introduced, aiming to bridge the gap between ceria and perovskite oxide-based materials by overcoming their individual thermodynamic constraints. Thermochemical CO<sub>2</sub> splitting redox cyclability of LSC25M75 evaluated with a thermogravimetric analyzer and an infrared furnace reactor over 100 consecutive redox cycles demonstrates a twofold higher conversion extent to CO than one of the best Mn-based perovskite oxides, La0.60 Sr0.40 MnO3. Based on complementary in situ high temperature neutron, synchrotron X-ray, and electron diffraction experiments, unprecedented structural and mechanistic insight is obtained into thermochemical perovskite oxide materials. A novel CO2 splitting reaction mechanism is presented, involving reversible temperature induced phase transitions from the n = 1 Ruddlesden–Popper phase (Sr<sub>1.10</sub>La<sub>0.64</sub>Ce<sub>0.26</sub>) MnO<sub>3.88</sub> (I4/mmm, K<sub>2</sub>NiF<sub>4</sub>-type) at reduction temperature (1350 °C) to the n = 2 Ruddlesden–Popper phase (Sr<sub>2.60</sub>La<sub>0.22</sub>Ce<sub>0.18</sub>)Mn<sub>2</sub>O<sub>6.6</sub> (I4/mmm, Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>-type) at re-oxidation temperature (1000 °C) after the CO<sub>2</sub> splitting step.

The solar thermochemical pathway utilizes the entire spectrum of concentrated solar radiation as the source of high temperature process heat to split CO2 and H<sub>2</sub>O into CO and H<sub>2</sub> (syngas), which is subsequently processed to synthetic liquid hydrocarbons, such as kerosene, diesel, or methanol, via the established Fischer-Tropsch synthesis and other gas-to-liquid processes.<sup>[3,4]</sup> The solar thermochemical splitting of CO<sub>2</sub> and H<sub>2</sub>O is performed via a two-step redox cycle, comprising: The endothermic reduction of a metal oxide at high temperatures (1400–1500 °C), generating lattice oxygen vacancies and resulting in O<sub>2</sub> evolution, followed by the exothermic re-oxidation of the reduced metal oxide with CO<sub>2</sub>/H<sub>2</sub>O at lower temperatures (800-1000 °C), generating CO/  $H_2$ .<sup>[2]</sup> The net reactions are  $H_2O = H_2 +$  $\frac{1}{2}O_2$  and  $CO_2 = CO + \frac{1}{2}O_2$ , but in contrast to direct thermolysis, the two-step cycle eliminates the need to separate the fuel  $(CO/H_2)$  and  $O_2$  at high temperatures.<sup>[5]</sup> A major challenge remains the discovery of a thermodynamically favorable and stable redox-active material which can be cycled at fast kinetic rates and exhibits high CO2 conversion extent. Thermo-

## **1. Introduction**

Solar-driven thermochemical (STC) technologies have the potential to generate carbon-neutral transportation fuels at the global scale, especially for the aviation and maritime sectors.<sup>[1,2]</sup>

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which in turn is dependent on the metal–oxygen bond dissociation energy, and the maximum reversible oxygen non-stoichiometry ( $\partial$ ).<sup>[6]</sup> Particularly, non-stoichiometric ceria (CeO<sub>2- $\partial$ </sub>)

dynamic studies suggest that the redox cyclability of a metal oxide is largely dependent on the oxide formation enthalpy,

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Perovskite-type oxides (ABO<sub>3- $\delta$ </sub>) have recently gained interest as an alternative class of redox materials for STC fuel production mainly due to their relative ease of reducibility at lower reduction temperatures compared to ceria (<1350 °C), their high structural tolerance to non-stoichiometry, tunable oxygen vacancy formation energetics, and their ability to accommodate a large variety of cations, thereby tuning point-defect thermodynamics.<sup>[10-12]</sup> However, these advantages are offset by unfavorable re-oxidation equilibria due to their low entropy change compared to pure ceria, leading to lower mass specific fuel productivity under most conditions relevant for STC cycles.<sup>[13]</sup> This causes the Gibbs free energy change of perovskites to be less sensitive to temperature changes, which necessitates operation at lower oxidation temperatures (<800 °C) or relatively large excess loads of CO2 gas flow (high CO2:CO molar ratio) for driving the thermodynamics of the re-oxidation step. However, this can result in higher energy penalties, consequently lowering the solar-to-fuel conversion efficiency.<sup>[14-16]</sup> Potential metal oxide  $(MO_r)$  redox materials should be able to split  $CO_2/H_2O$  with a high conversion extent to CO/H<sub>2</sub> (in case of a fed-batch reactor) or be tested under a low CO2:CO (H2O:H2) molar ratio flow conditions (in case of a flow-through reactor) to be classified as technologically attractive. A few material candidates resulted in a very low CO<sub>2</sub> (H<sub>2</sub>O) conversion extent, typically with a CO<sub>2</sub>:CO  $(H_2O:H_2)$  molar ratio  $\geq$ 1500:1 in the product stream<sup>[17-19]</sup> or in some other cases were tested at a very high oxidant to fuel ratio conditions with a CO<sub>2</sub>:CO (H<sub>2</sub>O:H<sub>2</sub>) ratio  $\geq$ 10000:1.<sup>[20]</sup> This often leads to overestimating the material's performance as the results would be substantially different at lower  $CO_2:CO$  (H<sub>2</sub>O:H<sub>2</sub>) molar ratios. In other words, the fuel quality would be impractical because of the low  $CO_2/H_2O$  conversion extent.

Lanthanum manganite based perovskite-oxides are the most intensely studied representatives in literature for STC two-step CO<sub>2</sub> splitting over a wide range of temperature and reaction conditions, and mainly Mn-containing perovskite oxides, such as,  $Sr_{x}La_{1-x}Mn_{v}Al_{1-v}O_{3-\delta}$  (LSMA)<sup>[21,22]</sup> and  $La_{0.60}Sr_{0.40}MnO_{3-\delta}$ (LSM)<sup>[12,23,24]</sup> have shown promise with high fuel yields (CO/ H<sub>2</sub>) during CO<sub>2</sub>/H<sub>2</sub>O splitting redox cycling experiments.<sup>[25]</sup> Density functional theory calculations and experimental studies by Deml et al. suggested that only oxides with oxygen vacancy formation energies  $(E_v)$  within a certain range (1.8–2.5 eV) are viable for STC fuel production, favoring both reduction and re-oxidation reaction thermodynamics.<sup>[22]</sup> Recently, Barcellos et al. reported a new perovskite-based oxide composite for thermochemical two-step water splitting, BaCe<sub>0.25</sub>Mn<sub>0.75</sub>O<sub>3</sub> (BCM) containing 12R and 10H polytypes, which demonstrated higher  $H_2$  yield compared to ceria when tested over different  $H_2O:H_2$ ratios, ranging from 1333:1 to 285:1 at a reduction temperature of 1350 °C and an oxidation temperature of 850 °C (using 0.1 g sample).<sup>[26]</sup> However, the structural parameters of the identified phases of the BCM composite material were not described, as the structure refinement of the in situ high temperature identified phases was not performed. This limits the understanding of the structural changes proceeding within the Ce-substituted

perovskite-oxide lattice under in situ high temperature reaction conditions. Moreover, it was reported that the BCM compound with mixed Ce/Mn occupancy at the B-site of the perovskite can only be formed with an exact composition of Ce (25%) and Mn (75%). Thus, the possibility to tune oxygen vacancy formation energetics through substitutional doping is restricted.<sup>[26]</sup> Generally, the lack of insight into the true phases and structure of perovskite oxide materials under STC operation conditions is a major conceptual roadblock for their targeted optimization.

To address these challenges, we synthesized and characterized a new perovskite oxide series with greater structural and compositional tunability by exploring the possibility of Ce-substitution at the B-site of lanthanum manganite-based perovskite oxides (referred to as LSCM series),  $La_{0.60-x}Sr_{0.40+x}(Ce_{\gamma}Mn_{1-\gamma})O_{3-\delta}$ , where the initial values are  $\gamma = 0$ , 0.10, 0.25, and 0.40 and  $x = 2\gamma$ ; denoted as pure LSM, LSC10M90, LSC25M75 and LSC40M60, respectively. We propose and substantiate that the mixed occupancy of Ce<sup>4+</sup> and Mn<sup>3+/4+</sup> at the B-site or Ce<sup>3+/4+</sup> at the A-site of the perovskite oxide lattice can induce significant octahedral structural distortions and offers the possibility to optimize metal oxygen bond strengths, thereby tuning oxygen vacancy formation energetics by just varying the composition.

In a limited number of studies, Ce-substituted perovskitetype oxides  $La_{1-x}Ce_xMO_3$  (M = Ni, Co, Fe, Mn) led to higher activity when tested for various catalytic reactions.<sup>[27-29]</sup> However, attempts to synthesize phase pure Ce-substituted perovskite oxide were largely unsuccessful and in most cases resulted in multiple phases with the presence of CeO<sub>2</sub> (fluorite) as an additional phase.<sup>[30,31]</sup> The low solubility of Ce atoms in the perovskite host lattice could be due to the low formation energy of the CeO<sub>2</sub> (fluorite) structure compared to most perovskite structures. Ganguly et al. studied structural and magnetic properties of La<sub>0.7</sub>Ce<sub>0</sub> 3MnO3 and confirmed that it can only form a multi-phase mixture with a hole doped La-deficient lanthanum manganate perovskite phase and CeO2.<sup>[32]</sup> In contrast, French et al. investigated charge defect mechanisms in  $La_{1-x}Ce_xCoO_{3-\delta}$  and identified that Ce4+ incorporation is indeed possible in an oxygen deficient lattice and concluded that the extent of Ce solubility in the lattice is dependent on the oxygen non-stoichiometry ( $\delta$ ) after exposure to high temperature preparation conditions.[33] Moreover, some uncertainties with respect to the Ce valence states and its crystallographic position in the perovskite host lattice remained.<sup>[34]</sup>

In this work, we synthesized a series of Ce-substituted (B-site) oxygen deficient lanthanum strontium manganite perovskite oxides (LSCM series) and tested them for thermochemical two-step CO<sub>2</sub>-splitting redox cycle performance. We present the first comprehensive structural study of a representative composition (LSC25M75) using complementary neutron, synchrotron X-ray, and electron diffraction techniques. Neutron diffraction refinement of pristine LSC2M75 sample at room temperature revealed the formation of a Mn-deficient perovskite oxide composite with the stoichiometry La<sup>3+</sup><sub>0.48</sub>Sr<sup>2+</sup>  $_{0.52}$ (Ce<sup>4+</sup> $_{0.06}$ Mn<sup>3+</sup> $_{0.79}$ )O<sub>2.55</sub> (*R-3c*), which has not been previously reported in literature. In addition, a minor second phase with disordered pyrochlore structure Ce4+2.6La3+1.4O6.28 (Fd-3m) is observed, which most likely exhibits a synergistic interaction with the main phase by not only serving as an oxide ion conductor (buffer layer) but also by possibly acting as an anti-sintering agent. The as-synthesized perovskite oxide composites



displayed remarkable oxygen exchange capacity (OEC) and long-term cyclic stability over 100 consecutive CO<sub>2</sub>-splitting redox cycles when tested using a thermogravimetric (TGA) analyzer and an infrared (IR) furnace reactor.

Furthermore, in situ high temperature neutron powder diffraction experiments were conducted to elucidate the structural and compositional dynamics of Ce-perovskite oxide composite materials, under near-operational conditions of the STC CO<sub>2</sub> splitting redox cycle. The structural refinement results of in situ high temperature neutron diffraction data together with ex situ synchrotron X-ray diffraction (XRD) of samples cooled down to room temperature (RT) after multiple CO<sub>2</sub> splitting redox cycling experiments elucidated a novel CO<sub>2</sub> splitting reaction mechanism for the thermochemical two-step CO<sub>2</sub> splitting redox cycle based on reversible phase transformations.

#### 2. Results and Discussion

#### 2.1. Thermogravimetric Redox Cycling Experiments

TGA redox cycling experiments were conducted to estimate the OEC ( $\Delta \delta$ ) of the target materials. The OEC is a trade-off between the energy required to break metal–oxygen bonds in the perovskite oxide lattice during the reduction and the energy released upon re-oxidation using CO<sub>2</sub> to restore these bonds, thereby reducing CO<sub>2</sub> to CO. The reduction extent or non-stoichiometry ( $\delta$ ) can be calculated from the following equation:

$$\delta = \frac{\Delta m}{m_{\rm s}} \times \frac{M_{\rm s}}{M_{\rm o}} \tag{1}$$

where  $\Delta m$  is the relative mass loss of the sample at equilibrium,  $m_{\rm s}$  is the sample mass taken,  $M_{\rm s}$  and  $M_{\rm o}$  are the molecular mass of sample and atomic oxygen, respectively. TGA cycling experiment plots of pure LSM, LSC10M90, LSC25M75, and LSC40M60 samples at various reduction and oxidation temperatures over 4 consecutive redox cycles are displayed in Figure S5(a), Supporting Information, and an additional zoomed plot of mass changes  $(\Delta m \%)$  during the second cycle is also shown in Figure S5(b), Supporting Information. The corresponding plot of calculated nonstoichiometry ( $\delta$ ) versus time curves of samples during the second cycle is shown in Figure 1. Pure LSM and ceria clearly represent the boundaries of reduction and oxidation extents of the LSCM compositional range. Wherein, pure LSM represents a lower boundary with its high reduction extent ( $\delta$ ) but a poor re-oxidation extent largely due to the thermodynamic limitations and ceria displays an upper boundary due to its rapid re-oxidation extent, while exhibiting a lower reduction extent ( $\delta$ ). The slope of the re-oxidation curve increases with the Ce-concentration in the LSCM series, along with a gradual decrease of the reduction extent ( $\delta$ ).

The LSC25M75 sample exhibits a good balance between high reducibility and rapid re-oxidation extent with a slope of its reoxidation curve almost twice as that of pure LSM. In contrast, samples with Ce-substitution at the A-site in  $(La_{0.6}Sr_{0.4-x}Ce_x)$  MnO<sub>3</sub> (x = 0.10, 0.20) did not show any significant improvement in their reduction and re-oxidation extents compared to the pure LSM and Ce-substituted (B-site) samples, as can be seen in Figure S8, Supporting Information.





**Figure 1.** TGA non-stoichiometry ( $\delta$ ) curves estimating the reduction and oxidation extent (2nd cycle) of the LSCM sample series versus ceria with reduction under Ar gas flow at 1350 °C (for 60 min) and oxidation under CO<sub>2</sub> at 1000 °C (for 80 min).

#### 2.2. Characterization of As-Synthesized Materials

Powder X-ray diffraction (PXRD) measurements of the entire series of Ce-substituted (B-site) samples at room temperature are shown in Figures S1 and S2, Supporting Information. Initial qualitative phase analysis revealed the presence of a main perovskite phase,  $La_{0.60-x}Sr_{0.40+x}(Ce_{\gamma}Mn_{1-\gamma})O_{3-\delta}$  with a rhombohedral (*R-3c*) structure along with the presence of a second phase accommodating excess Ce and La, with a Ce<sub>2+x</sub>La<sub>2-x</sub>O<sub>7- $\delta$ </sub> type pyrochlore (*Fd-3m*) structure (except for pure LSM). The percentage of pyrochlore (*Fd-3m*) phase increases with the nominal Ce concentration in the perovskite main phase.

Synchrotron XRD (25.0 keV) measurements of pure LSM, LSC10M90, and LSC25M75 samples were performed to precisely quantify phase composition, to determine lattice parameters, and to check for any impurity phases. The percentage phase compositions along with general stoichiometry of samples (at RT) pristine, post-TGA redox cycling (after the CO<sub>2</sub> splitting step) and post-high temperature reduction step (cooled under vacuum conditions) are shown in **Figure 2**. Rietveld refinement of synchrotron XRD patterns confirmed the substitution of 8% and 21% Ce at the B-site (Mn-site) of the main perovskite (*R-3c*) phase of the LSC10M90 and LSC25M75 pristine samples, respectively (**Figure 3**a).

However, XRD methods are not suitable to estimate the true occupancies of Ce/La and O atoms of the oxygen deficient perovskite (*R-3c*) oxide. This is mainly due to the inherent limitation of X-rays in accurately determining the oxygen atomic positions in an oxide containing heavy elements and its inability to distinguish neighboring elements (La, Ce) of the periodic table.<sup>[35]</sup> In addition, XRD could not probe the pyrochlore (*Fd-3m*) superstructure phase comprising La and Ce, and a defect fluorite (*Fm-3m*) structure was identified instead. This limitation of X-rays can be overcome by use of neutrons for diffraction.<sup>[36]</sup>

Neutron powder diffraction experiments of the composites were carried out in order to distinguish  $La^{3+}$  and  $Ce^{3+}/Ce^{4+}$  at





**Figure 2.** Phase composition and general stoichiometry of pure LSM, LSC10M90, and LSC25M75 samples pristine, post-TGA cycling (after the CO<sub>2</sub> splitting step) and post-high temperature reduction (cooled down under vacuum). The *I4/mmm* phase is a layered Ruddlesden–Popper phase, where n = 1 for the post-high temperature reduction samples and n = 2 for the post-TGA cycling (after CO<sub>2</sub> splitting) samples.

the A- and B-site of perovskite (*R-3c*) and pyrochlore (*Fd-3m*) phases and to determine positions and exact occupancies of La, Ce, Sr, Mn, and O atoms. Furthermore, in situ high-temperature neutron diffraction experiments (under vacuum conditions) were performed to investigate the material structure at reduction (1350 °C) oxidation (1000 °C) temperatures along with monitoring temperature-induced phase transitions and oxygen octahedral structural distortions.

The room temperature neutron diffraction refinement of LSC25M75 (pristine) is shown in **Figure 4**. The phase fraction percent and exact stoichiometry of both phases obtained from the refinement are Mn-deficient perovskite,  $(La^{3+}_{0.48}Sr^{2+}_{0.52})(Ce^{4+}_{0.06}Mn^{3+}_{0.79})O_{2.55}$  (*R-3c*, 68%) and pyrochlore Ce<sup>4+</sup><sub>2.6</sub>La<sup>3+</sup><sub>1.4</sub>O<sub>6.28</sub> (*Fd-3m*, 32%). The percent phase





**Figure 4.** Neutron powder diffraction refinement of LSC25M75 (pristine) at room temperature; upper tick marks La<sub>0.48</sub>Sr<sub>0.52</sub>(Ce<sub>0.06</sub>Mn<sub>0.79</sub>) O<sub>2.55</sub> (*R-3c*, 68%) *a* = 5.4776(3) Å, *c* = 13.3550(12) Å, *V* = 347.02(4) Å<sup>3</sup>, second row: Satellite reflections of the magnetic phase (*R-1*), third row: Ce<sub>2.6</sub>La<sub>1.4</sub>O<sub>6.24</sub> (*Fd-3m*, 32%) *a* = 11.0875(3) Å, *V* = 1363.01(6) Å<sup>3</sup>, and bottom: Nb sample container;  $R_{wp} = 9.29\%$ ,  $R_p = 6.94\%$ ,  $\chi^2 = 4.32$ .

fractions obtained from neutron and synchrotron XRD refinements agree well.

The pyrochlore  $Ce_{2+x}La_{2-x}O_{7-\delta}$  (*Fd-3m*) phase is known to act as a mixed oxide and electronic conductor in reducing atmospheres<sup>[37]</sup> and can possibly serve as a buffer layer to suppress cation interdiffusion.<sup>[38,39]</sup> This renders the phase very attractive for thermochemical  $CO_2$  splitting, so that we proceeded with detailed structural analyses and performance tests. The stoichiometry of each phase of the LSC25M75 composite derived from STEM-EDS elemental analysis (Table S1, Supporting Information) was used as a starting model for structural refinement. Particularly, the site occupancies of  $La^{3+}$  (48%) and  $Sr^{2+}$  (52%) were fixed at the A-site and the site occupancy of Ce, Mn (B-site), and the oxygen atoms of the *R-3c* phase were refined. Rietveld refinement results of the manganite phase revealed that it adopts a high symmetry oxygen deficient *R-3c* type-structure where 1/6th of the oxygen positions remain unoccupied. To maintain



**Figure 3.** Refinement of synchrotron XRD ( $\lambda$ =0.49297Å) data at room temperature on a) LSC25M75 (pristine), uppertick marks La<sub>0.48</sub>Sr<sub>0.52</sub>(Ce<sub>0.21</sub>Mn<sub>0.64</sub>)O<sub>3- $\delta$ </sub> (*R*-3*c*, 70%) and bottom Ce<sub>2.6</sub>La<sub>1.4</sub>O<sub>7- $\delta$ </sub> (*Fd*-3*m*, 30%) phase, b) LSC25M75 (post TGA), upper tick marks La<sub>0.48</sub>Sr<sub>0.52</sub>(Ce<sub>0.18</sub>Mn<sub>0.67</sub>)O<sub>3- $\delta$ </sub> (*R*-3*c*, 56%), middle Ce<sub>2.6</sub>La<sub>1.4</sub>O<sub>7- $\delta$ </sub> (*Fd*-3*m*, 26%), and bottom Sr<sub>2.60</sub>(La<sub>0.22</sub>Ce<sub>0.18</sub>)Mn<sub>2</sub>O<sub>7- $\delta$ </sub> (*Id/mmm*, 18%) phase.

2003532 (4 of 15)

electroneutrality, the proportion of overall occupancies at the Mn/ Ce site was thus reduced to perform further refinement steps.

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Neutron refinement of LSC25M75 (pristine) accurately confirmed the substitution of Ce<sup>4+</sup> ( $\approx$ 6%) and Mn<sup>3+</sup> ( $\approx$ 79%) at the B-site of the Mn-deficient perovskite (R-3c) phase. The neutron scattering lengths of Ce and Mn are of opposite signs, with Ce having a large positive neutron scattering length of +4.84 fm and Mn a large negative scattering length of -3.73 fm.<sup>[40]</sup> which renders this atomic combination suitable for good resolution of positions and site occupancies in neutron diffraction. The structural parameters obtained from the neutron diffraction refinement of LSC25M75 (R-3c phase) and of pure LSM (*R-3c* phase) at room temperature are given in Tables S2 and S3, Supporting Information. The refined lattice parameters of the *R-3c* main phase of LSC25M75 are a = 5.4776(3) Å and c =13.3550(12) Å, whereas those for pure LSM are a = 5.4802(1) Å and c = 13.3369(1) Å. This indicates an expansion of the rhombohedral lattice along the *c*-direction ( $\Delta c \approx 0.0181$  Å) in the Cesubstituted sample compared to the pure LSM sample. Upon closer examination, anisotropic atomic displacement parameters (U<sup>ij</sup>) of Mn and Ce at the 6b site (Table S2, Supporting Information) of LSC25M75 (R-3c phase) reveal the presence of significantly larger atomic disorder at the B-site of the perovskite lattice, compared to the U<sup>ij</sup> values of Mn atoms at the 6b site of pure LSM (Table S3, Supporting Information). This suggests that there may be a high degree of concerted atom movements (thermal) at the B-site, thus possibly facilitating expulsion of some Ce<sup>4+</sup>/Mn<sup>3+</sup> atoms from the B-site of a highly distorted perovskite (R-3c) structure of LSC25M75 at high temperatures. A plausible explanation for the unusual distortion of the MnO<sub>6</sub> octahedra (B-site) in LSC25M75 (R-3c) is the large difference in ionic radii of Ce4+ and Mn3+ atoms (ionic radii;

Ce<sup>4+</sup> (VI) = 0.87 Å, Mn<sup>3+</sup> (VI) = 0.645 Å).<sup>[41]</sup> It should be noted that the negative values of anisotropic atomic displacement parameters ( $U^{ij}$ ) of Ce/Mn (6b site) atoms (Tables S2 and S3, Supporting Information) could be linked to their opposing neutron scattering lengths resulting in either net zero or negative scattering lengths.

Bond valence sum (BVS) calculations also revealed a higher global instability index indicating a highly distorted perovskite structure. In addition, a decrease in the average Mn/Ce–O bond length of 1.9394(1) Å in LSC25M75 (*R-3c* phase) compared to the average Mn–O bond length of 1.9423(5) Å in pure LSM (*R-3c* phase) was observed (Table S4, Supporting Information). This suggests the presence of stronger Mn/Ce–O bonds in the Ce-substituted sample and provides a justification for a decrease in the reduction extent of LSC25M75 compared to pure LSM as observed in the TGA non-stoichiometry ( $\delta$ ) curve (Figure 1). Further, this demonstrates tunability of the OEC of perovskite oxide materials through compositional variation.

High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and electron diffraction patterns of a representative LSC25M75 sample (pristine) are displayed in **Figure 5**. The presence of two phases, rhombohedral (*R-3c*, P2) and pyrochlore (*Fd-3m*, P1), is evident from the electron diffraction patterns and from EDS elemental analysis. The particles of the *R-3c* and *Fd-3m* phases apparently form a grain boundary interface, thus facilitating diffusion of cations or oxygen ions between the two phases. STEM-EDS elemental analyses were carried out for each phase individually and the results are shown in Table S1, Supporting Information. The *R-3c* phase (P2 particle) displayed approx. atom% ratios of La:Sr = 48:52 at the A-site and of Ce:Mn =  $\approx 2-3\%$  to  $\approx 97-98\%$  at the B-site of the perovskite oxide lattice. In comparison, the *Fd-3m* 



**Figure 5.** HAADF-STEM images of a,d) LSC25M75 sample (pristine) at room temperature; b,c) representative atomic resolution STEM image and electron diffraction pattern of the P2 particle (*R-3c* phase) along the [100] zone axis; and e,f) representative atomic resolution STEM image and electron diffraction pattern of the P1 particle (*Fd-3m* phase) along the [100] zone axis.



**Figure 6.** STEM-EDS co-elemental distribution mapping of Ce (green) and Mn (yellow) atoms of the *R-3c* phase particles of a–c) the pristine LSC25M75 and d–f) post-TGA redox cycling samples.

(pyrochlore) phase (P1 particle) displayed an atom% fraction of Ce:La =  $\approx$ 65 to  $\approx$ 35% (Table S1, Supporting Information). The STEM-EDS derived elemental percentages were used to set up initial structural models for the refinement of neutron and synchrotron XRD data.

The overall elemental mappings across the two phases in LSC25M75 (pre- and post-TGA) are shown Figures S12 and S13, Supporting Information. Particularly, Ce and Mn elemental mapping of particles in pristine and post-TGA samples display Ce-rich (*Fd-3m*) and Ce-deprived (*R-3c*) regions with some overlap at the interface. In addition, co-elemental mapping of Ce and Mn of perovskite (*R-3c*) phase particles in pristine LSC25M75 and post-TGA samples point out atomic level mixing of Ce and Mn atoms even after numerous thermochemical CO<sub>2</sub> splitting redox cycles (**Figure 6**).

#### 2.3. Characterization under Reduction Conditions

In situ high temperature neutron powder diffraction measurements of pure LSM  $(La_{0.60}Sr_{0.40}MnO_{3-\delta})$  at a reduction

temperature of 1350 °C (under vacuum) show a complete transformation of the rhombohedral (R-3c) phase into a cubic (Pm-3m) phase in agreement with Tao et al.[42] (Figure S14, Supporting Information). However, an additional impurity phase of NbO (Pm-3m, ≈5%) was observed, possibly due to partial oxidation of the niobium sample container by lattice oxygen released from the perovskite oxide samples at high temperatures. Similarly, high temperature neutron powder diffraction refinement of the LSC25M75 composite revealed a phase transition from a room temperature rhombohedral (R-3c) phase to a cubic one (*Pm-3m*), along with the presence of a tetragonal (*I4/mmm*) phase. The pyrochlore Ce<sub>2.7</sub>La<sub>1.3</sub>O<sub>7</sub> (*Fd-3m*) phase observed at room temperature in pristine LSC25M75 was still present at high temperatures, albeit with a lower fraction (≤10%). The phase percent fractions, refined lattice parameters and stoichiometry of identified phases of the LSC25M75 composite at different temperatures are listed in Table 1.

At 1350 °C (reduction temperature), the Ce-substituted (B-site) distorted rhombohedral (*R-3c*) and pyrochlore (*Fd-3m*) phases of the LSC25M75 composite undergo a phase transition to a mixture of ( $Sr_{1.10}La_{0.64}Ce_{0.26}$ )MnO<sub>3.88</sub> (*I4/mmm*, 47%)

**Table 1.** Phase fraction, refined lattice parameters, and stoichiometry of each phase of a representative LSC25M75 composite material at reduction temperature 1350 °C, re-oxidation temperature 1000 °C, and after cooling down to 25 °C (RT) under vacuum conditions (derived from in situ high temperature neutron diffraction experiments).

Sample (in situ high temperature neutron diffraction exp.)	Stoichiometry	S.G.	Phase composition (wt%, ±2%)	Refined lattice parameters [Å]	
LSC25M75 at 1350 °C	(Sr <sub>1.10</sub> La <sub>0.64</sub> Ce <sub>0.26</sub> )MnO <sub>3.88</sub>	I4/mmm	47%	<i>a</i> = 3.9042(1), <i>c</i> = 13.2443(7)	
	La <sub>0.48</sub> Sr <sub>0.52</sub> MnO <sub>2.99</sub>	Pm-3m	41%	<i>a</i> = 3.9783(1)	
	Ce <sub>2.7</sub> La <sub>1.3</sub> O <sub>7</sub>	Fd-3m	12%	<i>a</i> = 11.2295(6)	
LSC25M75 at 1000 °C	(Sr <sub>1.18</sub> La <sub>0.60</sub> Ce <sub>0.20</sub> )MnO <sub>3.96</sub>	I4/mmm	67%	a = 3.8820(1), c = 13.2057(5)	
	La <sub>0.48</sub> Sr <sub>0.52</sub> MnO <sub>3</sub>	Pm-3m	25%	<i>a</i> = 3.9563(1)	
	Ce <sub>2.7</sub> La <sub>1.3</sub> O <sub>7</sub>	Fd-3m	8%	<i>a</i> = 11.1602(11)	
LSC25M75 after cooling down under vacuum (25 $^\circ$ C)	(Sr <sub>1.00</sub> La <sub>0.64</sub> Ce <sub>0.28</sub> )MnO <sub>3.64</sub>	I4/mmm	61%	<i>a</i> = 3.8303(1), <i>c</i> = 13.0300(5)	
	La <sub>0.48</sub> Sr <sub>0.52</sub> MnO <sub>2.85</sub>	Pm-3m	19%	<i>a</i> = 3.8911(5)	
	Ce <sub>2.82</sub> La <sub>1.18</sub> O <sub>7</sub>	Fd-3m	20%	<i>a</i> = 10.9954(15)	



and La<sub>0.48</sub>Sr<sub>0.52</sub>MnO<sub>2.99</sub> (*Pm-3m*, 41%) phases. The identified *I4/mmm* phase, Sr<sub>2-x</sub>(LaCe)<sub>x</sub>MnO<sub>4- $\delta$ </sub> is a K<sub>2</sub>NiF<sub>4</sub>-type<sup>[43]</sup> perovskite-related compound, which is a layered perovskite oxide of the general Ruddlesden–Popper series, A<sub>n+1</sub>B<sub>n</sub>O<sub>3n+1</sub> or AO(A<sub>1-x</sub>A'<sub>x</sub>BO<sub>3</sub>)<sub>n</sub> (where *n* = 1) consisting of alternate stacking of AO (rock salt) and ABO<sub>3</sub> (perovskite) layers along the c-axis as shown in Figure S16, Supporting Information. In general, these structures offer sufficient space in the AO layers to accommodate excess oxygen as interstitial atoms, while charge balance is maintained through oxidation of B-site cations. As such, these types of materials can act as highways for oxygen ion mobility and are therefore also well known for their mixed ionic-electronic conduction properties.<sup>[44,45]</sup>

The Rietveld refinement plot of in situ high temperature neutron powder diffraction of LSC25M75 at a reduction temperature of 1350 °C (under vacuum conditions) is shown in



**Figure 7.** a) In situ high temperature neutron diffraction refinement of the LSC25M75 composite at reduction temperature 1350 °C ( $R_{wp} = 4.87\%$ ,  $R_p = 3.60\%$ ,  $\chi^2 = 2.47$ ) and b) re-oxidation temperature 1000 °C ( $R_{wp} = 6.86\%$ ,  $R_p = 4.97\%$ ,  $\chi^2 = 2.54$ ); upper tick marks: *Pm-3m* phase, second row: *14/mmm* phase, third row: *Fd-3m* phase, the last two rows arise from NbO (<5%) and Nb sample holder, respectively. Phase fractions, refined lattice parameters, and stoichiometry of each phase are listed in Table 1.

**Figure** 7a. The refinement is satisfactory with lower R-values supporting the accuracy of the structural model and of the identified unknown phases at high temperatures. The refined structural parameters of the *I4/mmm* phase of LSC25M75 at 1350 °C derived from in situ high temperature neutron powder diffraction refinement are listed in Table S5, Supporting Information. It is only reasonable to include Ce atoms at the A-site of the *I4/mmm* phase of the *I4/mmm* phase of the *I4/mmm* phase for the high temperature structural refinements, because of the induced structural instability when large Ce- atoms are substituted at the B-site (octahedra) of perovskites.

The evolution of the I4/mmm phase at high temperatures can be accounted for by the Ce and Mn atoms migrating from the B-site of the distorted perovskite (*R-3c*) phase along with an equivalent proportion of Sr and La atoms being released from the A-site (to-maintain charge balance) of LSC25M75. In addition, the disordered pyrochlore (*Fd-3m*) phase also contributes to the formation of the *I4/mmm* phase at high temperatures.

The refined bond lengths (Å) of the second perovskite phase (*Pm-3m*) observed during in situ high temperature neutron diffraction of LSC25M75 are listed in Table S8, Supporting Information. In comparison to pure LSM ( $La_{0.60}Sr_{0.40}MnO_{3-\delta}$ , *Pm-3m*) at 1350 °C, the  $La_{0.48}Sr_{0.52}MnO_3$  (*Pm-3m*) phase of LSC25M75 at 1350 °C exhibits notably elongated La/Sr—O bond lengths, indicating a weaker A-site metal cation and oxygen bond strength. This may well render A-site metal–oxygen bonds in the latter susceptible to cleavage, resulting in a partial phase (*Pm-3m*) decomposition. BVS calculations also reveal an increase in the average manganese oxidation state of the *Pm-3m* phase from Mn +2.78 in pure LSM to Mn +3.22 in LSC25M75 at a reduction temperature of 1350 °C.

#### 2.4. Characterization under Re-Oxidation Conditions

Upon cooling down (under vacuum) the LSC25M75 composite from 1350 °C (reduction temperature) to 1000 °C (re-oxidation temperature) the fraction of the *I4/mmm* phase increases, resulting in a composition with stoichiometries and phase fractions of (Sr<sub>1.18</sub>La<sub>0.60</sub>Ce<sub>0.20</sub>)MnO<sub>3.96</sub> (*I4/mmm*, 67%) and La<sub>0.48</sub>Sr<sub>0.52</sub>MnO<sub>3</sub> (*Pm-3m*, 25%) phase (Table 1). Rietveld refinement plot of in situ high temperature neutron powder diffraction of LSC25M75 at a re-oxidation temperature of 1000 °C (under vacuum) is shown in Figure 7b. It is clear from the refined stoichiometries that the occupancy of oxygen atoms increased upon cooling down from 1350 to 1000 °C, indicating that additional oxygen atoms are accommodated in the layered perovskite (*I4/mmm*, K<sub>2</sub>NiF<sub>4</sub>-type) lattice.

It is worth mentioning that the *I4/mmm* phase is a major phase ( $\approx$ 70%) at the re-oxidation temperature of 1000 °C and plays a crucial role in explaining the enhanced CO<sub>2</sub> splitting ability of LSC25M75. As expected, the lattice parameters of all observed phases decreased after cooling down from 1350 to 1000 °C, due to the thermal contraction.

The refined structural parameters of the *I4/mmm* phase of LSC25M75 at 1000 °C derived from in situ high temperature neutron powder diffraction refinement are listed in Table S6, Supporting Information. Upon closer inspection, the anisotropic atomic displacement parameters ( $U^{ij}$ ) of oxygen atoms (O1) at the 4e site of (Sr<sub>1.18</sub>La<sub>0.60</sub>Ce<sub>0.20</sub>)MnO<sub>3.96</sub> (*I4/mmm*)



phase) at a re-oxidation temperature of 1000 °C display an abrupt increase compared to other atoms, besides a notable increase compared to the corresponding  $U^{ij}$  values of O1 atoms in (Sr<sub>1.10</sub>La<sub>0.64</sub>Ce<sub>0.26</sub>)MnO<sub>3.88</sub> (I4/mmm phase) at a reduction temperature of 1350 °C (Tables S5 and S6, Supporting Information). Especially striking are the larger  $U^{11}$  and  $U^{22}$  values (thermal displacement ellipsoids) for O1 at 1000 °C, which indicate a high degree of oxygen atomic disorder along the *ab*-plane, in contrast to its corresponding values at higher temperature of 1350 °C. Therefore, the bonds associated with O1 atomsmostly belonging to the AO (rock salt) layer of the I4/mmm phase—are more labile at re-oxidation temperatures (1000 °C) compared to those at reduction temperatures (1350 °C), thereby serving as a channel for oxide ion transport (O1 atoms are clearly marked and highlighted in Figure S16, Supporting Information). Furthermore, AO layers with highly disordered O1 atoms could also accommodate additional oxygen atoms and cations resulting in expansion of the layered perovskite structure by increasing the interlayer separation. On the other hand, all other atoms of the I4/mmm phase exhibit an expected decrease in U<sup>ij</sup> values upon cooling down from 1350 to 1000 °C.

Interatomic distances or bond lengths (in Å) of the *I4/mmm* phase at different temperatures derived from in situ high temperature neutron diffraction refinement of LSC2M75 are listed in Table S7, Supporting Information. The data reveal an increase in the Mn–O1(axial) interatomic distance at 1000 °C compared to that at 1350 °C. BVS calculations of Mn octahedra of the *I4/mmm* phase at different temperatures also reveal an increase in the average manganese oxidation state from Mn +2.73 at 1350 °C (reduction temperature) to Mn +2.88 upon cooling down to 1000 °C (re-oxidation temperature). This increase can be attributed to the increasing concentration of Jahn–Teller distorted Mn(III) atoms at the octahedral sites, thereby extending the axial Mn–O1 bonds (Figure S16, Supporting Information). This extension can force AO (rock salt) layers apart, resulting in an increasing interlayer separation.

#### 2.5. Characterization after Cooling Down

Neutron diffraction experiments of the LSC25M75 composite after cooling down (under vacuum) from 1000 to 25 °C (RT) revealed a phase composition of  $(Sr_{1.00}La_{0.64}Ce_{0.28})MnO_{3.64}$  (*I4/mmm*, 61%),  $La_{0.48}Sr_{0.52}MnO_{2.85}$  (*Pm-3m*, 19%), and  $Ce_{2.82}La_{1.18}O_7$  (*Fd-3m*, 20%) (Table 1). The space group symmetry of all the phases remain unchanged even after cooling down to RT, with *I4/mmm* (*n* = 1) phase being present as a major phase. The Rietveld refinement plot of LSC25M75 after cooling down from in situ high temperature experiments under vacuum conditions is shown in Figure S15, Supporting Information.

Furthermore, synchrotron XRD of LSC25M75 post-TGA redox cycling provided crucial information for deriving a possible reaction mechanism of the CO<sub>2</sub> splitting step during thermochemical redox cycling experiments. Synchrotron XRD patterns of LSC25M75 were recorded at room temperature on a sample which had been previously exposed to numerous thermochemical CO<sub>2</sub> splitting cycles (10 cycles,  $\approx 26$  h) and was cooled down under high Ar gas flow ( $p_{O2} \approx 10^{-5}$  atm) conditions from the re-oxidation temperature (1000 °C). Rietveld

refinement of LSC25M75 (post-TGA CO<sub>2</sub> splitting) resulted in a phase composition (Figure 3b) of La<sub>0.48</sub>Sr<sub>0.52</sub>(Ce<sub>0.06</sub>Mn<sub>0.94</sub>)O<sub>3</sub> (*R*-3*c*, 56%), Ce<sub>2.7</sub>La<sub>1.3</sub>O<sub>7</sub> (*Fd*-3*m*, 26%), and Sr<sub>2.60</sub>(La<sub>0.22</sub>Ce<sub>0.18</sub>) Mn<sub>2</sub>O<sub>7</sub> (*I4/mmm*, 18%) (Figure 2). Surprisingly, the rhombohedral (*R*-3*c*) phase (as identified in pristine samples) re-appeared as a major phase, with Ce (≈6%) re-substituted at the B-site of the perovskite structure. Most of the *I4/mmm* (≈67%) and *Pm*-3*m* (25%) phase fractions present during the in situ high temperature neutron diffraction experiment seem to reversibly transform into rhombohedral (*R*-3*c*) and pyrochlore (*Fd*-3*m*) phases. However, about 18% of *I4/mmm* phase was left possibly due to incomplete re-oxidation of the sample during the CO<sub>2</sub> splitting step. It is worth noting that the pyrochlore (*Fd*-3*m*) phase fraction (≈26%) was restored approx. to the initial percentage as in the pristine LSC25M75.

The refinement plot of room temperature synchrotron XRD data for LSC25M75 (post-TGA CO<sub>2</sub> splitting) is shown in Figure 3b and the resulting structural parameters of the I4/mmm phase are listed in Table S9, Supporting Information. The lattice parameters of the I4/mmm phase of LSC25M75 (post-TGA CO<sub>2</sub> splitting) revealed a large expansion along the *c*-direction with a = 3.8623(1) Å, c = 20.400(1) Å, in comparison to the in situ high temperature I4/mmm phase at 1000 °C with a = 3.8820(1)Å, c = 13.2057(5) Å. Rietveld refinement of the I4/mmm phase of LSC25M75 (post-TGA CO<sub>2</sub> splitting) unraveled that it adapts a Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>-type structure,<sup>[46]</sup> which indeed is also a member of the Ruddlesden–Popper series (with n = 2), wherein an additional layer of BO<sub>6</sub> octahedra is joined along the stacking direction (c-axis) and separated by rock salt (AO) layers (Figure S16b, Supporting Information). It should be noted that only isotropic atomic displacement parameters (Uiso) were refined for XRD data of LSC25M75 post-TGA redox cycling, as neutron diffraction would be necessary for the refinement of anisotropic atomic displacement parameters  $(U^{ij})$  refinement. In addition, the inherent limitation of X-rays in accurately identifying oxygen atom positions resulted in a slight discrepancy in oxygen occupancies and could possibly account for the negative U<sub>iso</sub> value at the Mn (4e) site (Table S9, Supporting Information).

#### 2.6. Reaction Mechanism

The results of the in situ high temperature neutron powder diffraction experiments at temperatures relevant for STC fuel production reactors, along with ex situ synchrotron XRD data of pre- and post-TGA redox cycling samples, provided the first experimental evidence to date for deriving a thermochemical CO<sub>2</sub> splitting reaction mechanism of Ce-based perovskite oxide composite materials. For the first time, we provide detailed structural parameters (including the monitoring of oxygen vacancies) of each phase of the sample derived from in situ neutron diffraction refinement at high temperature reduction (1350 °C), re-oxidation (1000 °C) temperatures and after cooling down (25 °C), wherein phase composition, stoichiometry, and structural changes of the materials were probed at each stage of the thermochemical redox cycles. The schematic summary of in situ high temperature neutron diffraction and synchrotron XRD experiments of the LSC25M75 composite material along with the stoichiometry of each identified phase at different



Figure 8. Schematic summary of the in situ thermochemical redox cycling experiments along with details of experimental conditions applied at each step for deriving structural parameters from neutron and synchrotron X-ray diffraction experiments.

stages (stage 1 to 4) of the thermochemical two-step  $CO_2$  splitting redox cycle are shown in Figure 8.

In particular, the presence of the major I4/mmm phase ( $\approx 67\%$ ) at re-oxidation temperatures seems to be mainly responsible for the enhanced CO<sub>2</sub> splitting ability of LSC25M75 composite. The structure of the I4/mmm phase, Sr2-x(LaCe)xMnO4-& derived from the refinement of in situ high temperature neutron diffraction experiments at 1350 and 1000 °C (under vacuum conditions), is a K<sub>2</sub>NiF<sub>4</sub>-type layered perovskite oxide belonging to the Ruddlesden–Popper series (n = 1). Furthermore, metal oxygen bonds associated with the AO (rock salt) layers of the I4/mmm phase (K<sub>2</sub>NiF<sub>4</sub>-type) at 1000 °C appear to be more labile than the corresponding ones at 1350 °C (Tables S5 and S6, Supporting Information), consequently expanding the layered perovskite structure by accommodating additional cations from the partially decomposed *Pm-3m* phase. Thus, the Pm-3m phase of LSC25M75 seem to act as a cation reservoir for the Ruddlesden-Popper structural expansion of the I4/mmm phase at the re-oxidation temperature (1000 °C).

Synchrotron XRD measurements of LSC25M75 post-TGA  $CO_2$  splitting redox cycles ( $\approx 26$  h), followed by cooling down to room temperature under high Ar gas flow conditions (Figure 8, stage 4), provided crucial information for understanding the structure of the material at near operational conditions, i.e., re-oxidation temperature (1000 °C) under CO<sub>2</sub> gas flow conditions. Structural analysis and refinement of LSC25M75 (post-TGA redox cycling) revealed an interesting reversible phase transformation of the high temperature I4/mmm and Pm-3m phases back to the R-3c phase, along with restoration of the Fd-3m phase to almost identical phases and compositions as in pristine LSC25M75. The phase fractions and stoichiometries derived from refinement of LSC25M75 (post-TGA redox cycling) are La<sub>0.48</sub>Sr<sub>0.52</sub>(Ce<sub>0.18</sub>Mn<sub>0.67</sub>)O<sub>2.66</sub> (R-3c, 56%), Ce<sub>2.7</sub>La<sub>1.3</sub>O<sub>7</sub> (Fd-3m, 26%), and Sr<sub>2.60</sub>(La<sub>0.22</sub>Ce<sub>0.18</sub>)Mn<sub>2</sub>O<sub>7</sub> (I4/mmm, 18%). Especially, the structural comparison of the residual I4/mmm phase in LSC25M75 (post-TGA redox cycling) to the I4/mmm phase of LSC25M75 during in situ high temperatures (under vacuum) revealed an interesting phenomenon. The residual I4/mmm phase (in LSC25M75 post-TGA redox cycling), adapts the Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> (n = 2) type-structure, which is also a member of Ruddlesden–Popper phase layered perovskite oxide series, with an additional stacking layer of BO<sub>6</sub> octahedra separating the AO (rock salt) layers along the *c*-direction. This expansion is compensated by accommodating additional cations, namely La, Sr, Mn (sourced from the *Pm-3m* phase), and oxygen atoms (from CO<sub>2</sub> splitting) in between AO interlayers of the high temperature *I4/mmm*, K<sub>2</sub>NiF<sub>4</sub> (n = 1) type-structure at the re-oxidation temperature of 1000 °C.

Based on all in situ high temperature neutron and ex situ synchrotron XRD experiments, we propose a possible overall reaction mechanism depicting temperature induced reversible phase transformations during the two-step thermochemical CO<sub>2</sub> splitting redox cycling of LSC25M75 as shown in **Figure 9**.

It should be noted that the refined crystal structure of the I4/mmm phase (Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>-type) shown in the reaction mechanism scheme is a residual phase (≈18%) after cooling down from the CO<sub>2</sub> splitting step (i.e., re-oxidation temperature 1000 °C). Moreover, it is reasonable to predict that most of the I4/mmm phase (K<sub>2</sub>NiF<sub>4</sub>-type) fraction ( $\approx$ 67%) observed during in situ high temperature neutron experiments at 1000 °C (under vacuum) reversibly transforms into the I4/mmm phase (Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>-type) upon exposure to CO<sub>2</sub> gas during re-oxidation temperatures. In addition, the IR-furnace reactor experiments of LSC5M75 over 100 thermochemical CO<sub>2</sub> splitting redox cycles (Figure 11) point out a gradual increase in CO production rate with cycle number. This could be due to slow phase transformations, wherein the percentage of the *I4/mmm* phase (n = 2)increases with the cycle number. Therefore, we propose that it would most likely require a longer time of on-stream gas flow under high temperature thermochemical redox cycle conditions to eventually reach the maximum achievable reversible phase fraction of  $Sr_{2.60}(La_{0.22}Ce_{0.18})Mn_2O_{6.6}$  (I4/mmm, n = 2, 67%). It is also worth mentioning that these phases are generated only under in situ high temperature conditions (under vacuum) and hence decompose back to their original phase compositions as soon as the sample is cooled down to 25 °C (RT).

Another intriguing observation from the refined crystal structure of the *I4/mmm* phase (Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>-type) in LSC25M75





**Figure 9.** Schematic overall reaction mechanism of two-step thermochemical CO<sub>2</sub> splitting redox cycling derived from in situ high temperature neutron and ex situ synchrotron X-ray powder diffraction experiments of the LSC25M75 composite. The reaction mainly proceeds via a reversible temperature induced phase transition from the n = 1 (K<sub>2</sub>NiF<sub>4</sub> -type) to the n = 2 (Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> -type) Ruddlesden–Popper layered perovskite oxides (green = Sr/La/Ce, magenta = Mn, red = O). The bonds assocated with the O1 atoms (highlighted) of AO rock salt layers are more labile. The *Pm-3m* phase acts a cation reservoir phase, while O atoms arise from the CO<sub>2</sub> splitting.

(post-TGA) is the presence of partially oxidized  $MnO_6$  octahedra with oxygen vacancies mostly linked to the AO (rock salt) layers (Figure 9). This is possibly due to incomplete re-oxidation of the sample during the  $CO_2$  splitting step resulting in a transformation of  $MnO_6$  octahedra into a  $MnO_5$  square-pyramidal coordination environment.

Finally, the presence of the pyrochlore Ce<sub>2.6</sub>La<sub>1.4</sub>O<sub>6.28</sub> (*Fd-3m*) phase also plays an important role in enhancing the CO<sub>2</sub> splitting ability of the LSC25M75 perovskite composite material. Pyrochlore oxides  $(A_2B_2O_7)$  are known to be used for a wide range of technological applications, including their utilization as electrolytes in solid oxide fuel cells and as thermal barrier coatings.<sup>[39,47]</sup> However, the crystal structure of these materials still remains controversial, and two models based on disordered defect fluorite (Fm-3m) and pyrochlore (Fd-3m) type are mainly considered, depending on the concentration of B-site cations and the ionic radii ratio of the A and B cations  $(r_A/r_B)$ .<sup>[37,48,49]</sup> The general composition of the identified pyrochlore phase is  $Ce_{1-x}La_xO_{2-x/2}$  (where x = 0.35, 0.40) with  $La^{3+}$  at the A-site and  $Ce^{4+}$  at the B-site and  $r(La^{3+})/r(Ce^{4+}) = 1.3$ , resulting in a large lattice distortion. Neutron diffraction experiments of the LSC25M75 composite revealed the presence of a disordered pyrochlore  $Ce_{2,6}La_{1,4}O_{7-\delta}$  (*Fd-3m*) structure, which is analogous to a 2 × 2 × 2 superstructure of the disordered defect fluorite  $Ce_{0.65}La_{0.35}O_{2-\delta}$ (Fm-3m) type with 1/8 of the oxygen positions on the 8a site being vacant. According to the literature, the  $Ce_{0.60}La_{0.40}O_{2-\delta}$ phase is known to act as a buffer layer to prevent cation interdiffusion between perovskite phase particles during high temperature reaction conditions, by selectively permitting oxygen ion migration.<sup>[37,50]</sup> Furthermore, these pyrochlore (Fd-3m) phases are widely used as a high temperature resistant materials and can possibly act as anti-sintering agents.<sup>[38,39]</sup> Sintering of particles can exert a detrimental effect on the CO<sub>2</sub> splitting ability of materials during long term thermochemical redox cycling experiments. SEM images of LSC25M75 pre- and post- TGA redox cycling experiments (10 cycles) revealed no significant

sintering or grain growth of particles even after numerous thermochemical CO<sub>2</sub> splitting cycles ( $\approx$ 26 h) as shown in Figure S17, Supporting Information. Therefore, the pyrochlore (*Fd-3m*) phase seems to exhibit a synergistic interaction with the perovskite (*R-3c*) main phase of the LSC25M75 composite by not only contributing to the formation of *I4/mmm* major phase at high temperature reaction conditions, but also by being possibly responsible for the anti-sintering stability of the material.

#### 2.7. Infrared-Furnace Reactor Redox Cycling Experiments

The long-term reactive stability and durability of the new perovskite oxide composite materials were tested using an IR-furnace reactor over 100 thermochemical CO<sub>2</sub> splitting redox cycles. The schematic experimental setup of the IR-furnace reactor (VHT-E48, Ulvac-Riko)<sup>7,8</sup> is displayed in Figure S18, Supporting Information. Initially, materials (≈2 g, 8 mmol) performance was evaluated at various reduction (1300, 1350, and 1400 °C), oxidation (800, 900, and 1000 °C) temperatures, CO2 gas partial pressures (CO2 to Ar ratios) and different durations (in min) of reduction and oxidation reactions over three consecutive redox cycles. The optimal testing conditions derived were then used for long term thermochemical two-step CO<sub>2</sub> splitting redox cycling experiments; reduction  $T_{\rm red} = 1350$  °C,  $V_{\rm Ar} = 0.5$  L min<sup>-1</sup>,  $t_{\rm red} = 3$  min, and re-oxidation  $T_{\rm oxi} = 800$  °C,  $V_{\rm CO2} = 0.5$  L min<sup>-1</sup>,  $t_{\rm oxi}$  = 4.5 min. The rationale behind the choice of these experimental conditions was to maximize the gas detection signal to noise ratio, as well as to reach the threshold gas detection limit of individual gas detector components of the Ultramat gas analyzer.

In order to analyze the data, it is convenient to define the extent of  $CO_2$  conversion to CO or mole fraction of CO ( $X_{CO}$ ), given by,

$$X_{\rm CO} = \frac{n_{\rm CO}}{(n_{\rm CO} + n_{\rm CO2})}$$
(2)

2003532 (10 of 15)



where  $n_{CO}$  and  $n_{CO2}$  are number of moles of CO produced and CO<sub>2</sub> injected, respectively, during the re-oxidation step. In addition to the requirement of high CO production rates during the re-oxidation step, potential redox metal oxides (MO<sub>x</sub>) should be able to split CO<sub>2</sub> with high conversion extents to CO  $(X_{CO})$  in case of a fed-batch reactor or be tested using low CO<sub>2</sub>:CO molar ratio flow stream conditions in case of a flow-through reactor to be technically feasible. The representative CO production data of the initial two CO<sub>2</sub> splitting cycles (excluding the 1st cycle) for LSM, LSC25M75 and pure ceria are shown in Figure S19, Supporting Information. Each sample was subjected to an initial reduction step from a fully oxidized state followed by three complete CO<sub>2</sub> splitting cycles, and each cycle comprised of a reduction step followed by a subsequent re-oxidation step. The initial CO production yield per cycle of LSC25M75  $(103 \pm 4 \,\mu\text{moles}/0.01 \text{ mol sample})$  is much larger than that of pure LSM (72  $\pm$  4  $\mu$ moles/0.01 mol sample). The peak rate of CO production of LSC25M75 ( $\approx 0.8 \ \mu moles \ s^{-1}$ ) is almost twice that of pure LSM ( $\approx 0.4 \ \mu moles \ s^{-1}$ ). For comparison, the stateof-the art material pure ceria (CeO<sub>2</sub>) displayed a CO production yield of  $110 \pm 2 \,\mu$ moles/0.01 mol sample/cycle as shown in Figure S19, Supporting Information. Ceria exhibits a large conversion extent and sufficiently fast reaction kinetics with a sharp CO evolution peak, whereas the LSC25M75 sample (and LSM) shows a very broad CO production peak indicating that the CO<sub>2</sub> splitting step is thermodynamically (and kinetically) unfavorable compared to ceria. This is mainly because of low entropy changes ( $\Delta S$ ) of perovskites compared to ceria, thereby requiring either larger temperature swings ( $\Delta T$ ) or large excess CO<sub>2</sub> flow loads (i.e., very high CO<sub>2</sub>:CO ratio) to drive the Gibbs free energy change ( $\Delta G$ ) of the oxidation step toward negative or zero. Zhai et al. reported that  $La_{0.6}Sr_{0.4}MnO_{3-\delta}$  perovskites have a critical CO<sub>2</sub>:CO conversion ratio of 650:1 at  $T_{red}$  = 1300 °C and  $pO_2 = 10^{-5}$  atm, and  $T_{oxi} = 800$  °C indicating a very low conversion extent and using a lower CO<sub>2</sub> molar gas flow rate than critical (CO2:CO) ratio would result in negligible or zero CO vield.<sup>[51]</sup>

Reactive stability and cyclability of thermochemical twostep CO<sub>2</sub> splitting of pure LSM, LSC25M75 and ceria samples were tested over 20 redox cycles to evaluate the performance of materials under realistic conditions of radiative heating. LSC25M75 (1-20 cycles) displays almost 1.5 times higher average CO and O2 production yields with  $115 \pm 4 \mu$ moles CO/cycle (with an average molar conversion ratio of CO<sub>2</sub>:CO = 871:1) and 80  $\pm$  20  $\mu$ moles O<sub>2</sub>/cycle respectively, compared to pure LSM (1-20 cycles) with corresponding average values of 78  $\pm$  4  $\mu$ moles CO/cycle (with a lower average molar conversion ratio of CO<sub>2</sub>:CO = 1285:1) and  $54 \pm 15 \,\mu$ moles  $O_2$ /cycle as shown in **Figure 10**. The amount of  $O_2$  released in each cycle is not exactly half of the CO produced, this could be attributed to the different detection mechanisms and their accuracies. It should be noted that the  $O_2$  peak integrals are overestimated because the lower detection limit of the oxygen sensor is reached, thus contributing to a significant error in the average  $O_2$  production values.

The CO production rates of LSC25M75 (1–20 cycles) seem to gradually increase with cycle number in contrast to pure LSM and ceria which displayed a stable performance over 20 cycles. Both LSC25M75 and pure LSM release a much





**Figure 10.** Long term reactive stability and cyclability experiments of thermochemical two-step  $CO_2$  splitting redox reaction on a) LSC25M75 (1–20 cycles), b) LSC25M75 (70–100 cycles), and c) pure LSM (1–20 cycles). The CO and  $O_2$  production plots of LSC25M75 (20–70 cycles) are shown in Figure S21, Supporting Information.

higher oxygen content than ceria during the initial reduction step, which however drops down to a significantly lower value ( $\approx 60-70\%$  of initial cycle O<sub>2</sub> value) during subsequent cycles. This is mainly due to the thermodynamic and kinetic limitation of the CO<sub>2</sub> splitting reaction during re-oxidation of perovskite oxides and suggests an incomplete re-oxidation

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Ceria

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Material	Average CO production yield (μmoles CO/cycle/0.01 mol sample)	Average CO <sub>2</sub> :CO molar conversion ratio	Average CO <sub>2</sub> conversion extent (X <sub>CO</sub> )	Peak CO <sub>2</sub> conversion extent (X <sub>co</sub> _peak)	$\delta/{ m total}$ stoichiometry
Pure LSM	78 ± 4	1285:1	7.77E-4	1.21E-3	15.60
LSC25M75(1–20 cycles)	115 ± 4	871:1	1.14E-3	2.23E-3	19.34
LSC25M75(70–100 cycles)	142 ± 4	706:1	1.42E-3	2.61E-3	23.88

186.1

**Table 2.** Summary of IR furnace experiment results of samples including values of average  $CO_2$ :CO molar conversion ratio, average  $CO_2$  conversion extent ( $X_{co}$ ), peak  $CO_2$  conversion extent ( $X_{co}$ ), peak  $CO_2$  conversion extent ( $X_{co}$ ), and  $\delta$ /total stoichiometry.

of the sample. In other words, the allotted time during the CO<sub>2</sub> splitting step is not enough to completely re-oxidize the perovskite oxide, which was chosen to approximate the cycle times associated with that of a real STC CO<sub>2</sub> splitting reactor. Ceria, on the other hand, when tested under similar conditions shows a large conversion extent and rapid reaction kinetics with almost the same CO production yield of  $120 \pm 2 \,\mu$ moles/cycle (with an average molar conversion ratio CO<sub>2</sub>:CO = 186:1), O<sub>2</sub> production yield of  $74 \pm 15 \,\mu$ moles/cycle and stable rates over 20 cycles as shown in Figure S20b, Supporting Information.

120 + 2

The results of IR-furnace experiments of pure LSM, LSC25M75 and ceria are summarized in **Table 2**, including values of average CO<sub>2</sub>:CO molar conversion ratio, average CO<sub>2</sub> conversion extent ( $X_{co}$ ), peak CO<sub>2</sub> conversion extent ( $X_{co}$ -peak) and  $\delta$ /total stoichiometry.

LSC25M75 (70-100 cycles) displayed a peak molar CO<sub>2</sub> to CO conversion extent of 0.26% which is about two times larger than the peak molar conversion extent of pure LSM of 0.12%, whereas ceria has a peak molar conversion extent of 2%, when tested under similar conditions of mass flow rate of CO<sub>2</sub> = 0.5 L min<sup>-1</sup>,  $T_{\rm oxi}$  = 800 °C,  $T_{\rm red}$  = 1350 °C, and  $P_{\rm total}$  = 1 bar, sample mass = 2 g ( $\approx 0.01$  mol). The CO<sub>2</sub> conversion extent  $(X_{co})$  is calculated only for the duration where the reaction is actually happening, for example, ceria has completely re-oxidized in about 1.5 min out of 4.5 min of allotted re-oxidation time, whereas LSM and LSC25M75 have not been able to completely re-oxidize even after 4.5 min of re-oxidation. The peak CO conversion extent of each sample is the measured highest instantaneous CO<sub>2</sub> molar conversion to CO. The ratio  $\delta$ /(total stoichiometry) is a standard way to measure or compare redox extents ( $\Delta \delta$ ) of samples with different stoichiometries. The value is a measure of oxygen vacancies relative to the total number of moles of atoms in a reactive solid material. This normalization helps to deal with the specific heat capacity  $(c_p)$  of materials and provides an estimate of oxygen absorbed relative to the energy needed to cycle the materials between reduction and oxidation temperatures. Furthermore, long term stability testing of LSC25M75 was extended to 100 redox cycles aiming to determine the maximum possible CO peak production rates per cycle (Figure S21, Supporting Information). The LSC25M75 composite displayed not only a stable performance but also a gradual increase in CO and O<sub>2</sub> production rates along with higher yields over 100 redox cycles. The experimental plots of LSC25M75 (1-20 cycles) displayed a gradual increase in average CO and O<sub>2</sub> production yield per cycle from 115  $\pm$  4 µmoles CO/cycle (average molar CO<sub>2</sub>:CO = 871:1) to 142  $\pm$  4 µmoles CO/cycle (average CO<sub>2</sub>:CO = 706:1) in

LSC25M75 (70–100 cycles) as shown in Figure 10. This can be attributed to slow phase transitions in LSC25M75 during the high temperature reaction conditions, wherein the percentage of reactive Ce-substituted perovskite (*I4/mmm* phase) gradually increases with cycle number. On the other hand, the observed drift in the O<sub>2</sub> production peaks of LSC25M75 (40–100 cycles) (Figure 10 and Figure S21, Supporting Information) could be due to oversaturation of the electrochemcial O<sub>2</sub> sensor. This can happen in the event of sudden changes from high O<sub>2</sub> concentrations (>20 vol%) to low O<sub>2</sub> concentrations (<1 vol %), such as when synthetic air is used for re-oxidation of the samples or for the calibration of the sensor. In this case the sensor requires longer running-in times to obtain a constant measured value. This also accounts for the observed uncertainty in the O<sub>2</sub> production measurements.

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The average CO and O<sub>2</sub> production yields ( $\mu$ moles/ cycle/0.01 mol sample) of LSC25M75 over 100 redox cycles were compiled and presented in **Figure 11**, wherein each cycle lasts for  $\approx$ 15 min.

Overall, LSC25M75 (70–100 cycles) displayed two times higher CO<sub>2</sub> conversion extent to CO (re-oxidation extent) than pure LSM ( $La_{0.60}Sr_{0.40}MnO_{3-\delta}$ ) when tested over 100 thermochemical redox cycles. The main performance difference between the materials could be largely due to their thermodynamic limitations rather than their kinetic limitations<sup>[13]</sup> (or a combination of both limitations).



**Figure 11.** CO and O<sub>2</sub> production yields per each cycle (in  $\mu$ moles/cycle) of LSC25M75 over 100 consecutive thermochemical CO<sub>2</sub>-splitting redox cycles tested in the IR-furnace reactor.



## 3. Conclusions

Novel Ce-substituted lanthanum strontium manganite perovskite oxide composite materials were synthesized and their OEC for thermochemical two-step CO<sub>2</sub> splitting redox cycles was explored. A wide range of structural characterizations demonstrate that Mn<sup>3+</sup> was successfully replaced with Ce<sup>4+</sup> at the B-site of La<sub>0.48</sub>Sr<sub>0.52</sub>(Ce<sub>0.06</sub>Mn<sub>0.79</sub>)O<sub>2.55</sub> (LSC25M75). LSC25M75 exhibited two times higher CO2 conversion extent compared to pure LSM (one of the best perovskite oxides for STC-fuel production) during TGA redox cycling and IR-furnace reactor experiments. To elucidate the reasons for this enhanced performance, the first comprehensive structural study of the LSC25M75 composite material was carried out with a combination of in situ high temperature neutron, synchrotron X-ray and electron diffraction experiments. Neutron diffraction refinement of pristine LSC25M75 at room temperature accurately provided its phase composition and revealed the formation of a Mn deficient perovskite oxide La<sub>0.48</sub>Sr<sub>0.52</sub>Ce<sub>0.06</sub>Mn<sub>0.79</sub>O<sub>2.55</sub> (R-3c, 70%), along with the presence of a pyrochlore phase Ce<sub>2.6</sub>La<sub>1.4</sub>O<sub>6.28</sub> (Fd-3m, 30%). Furthermore, structural refinements of in situ high temperature neutron powder diffraction patterns together with ex situ synchrotron XRD experiments of pre- and post-TGA redox cycling samples provided unprecedented experimental evidence about the actual structure of perovskite oxide composite materials at temperatures relevant for thermochemical fuel production redox cycles. These insights hold the key to the first coherent proposal of a thermochemical two-step CO<sub>2</sub> splitting reaction mechanism of Ce-perovskite oxide composites.

Rietveld refinement results of in situ high temperature neutron diffraction experiments of the LSC25M75 composite at 1350 and 1000  $^\circ C$  revealed a phase transition from a room temperature rhombohedral (R-3c) phase with Ce substituted at the B-site to a tetragonal (Sr<sub>1.18</sub>La<sub>0.60</sub>Ce<sub>0.20</sub>)MnO<sub>3.96</sub> (I4/mmm) layered perovskite oxide phase with Ce substituted at the A-site and a cubic La<sub>0.48</sub>Sr<sub>0.52</sub>MnO<sub>3</sub> (Pm-3m) phase. In situ high temperature neutron diffraction of LSC2M75 at 1350 and 1000 °C (under vacuum) and synchrotron XRD of the same sample cooled down (under high Ar flow) from the re-oxidation temperature 1000 °C and after exposure to numerous CO2-splitting redox cycles revealed an interesting reversible structural transformation, that is, from the I4/mmm phase (K<sub>2</sub>NiF<sub>4</sub>-type) to an expanded I4/mmm phase (Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>-type) upon re-oxidation during the CO<sub>2</sub> splitting step. Both of these I4/mmm phases are layered perovskite oxides of the Ruddlesden-Popper family with the general formula  $AO(A_{1-x}A'_{x}BO_{3})_{n}$ , with n = 1 for the former, and n = 2 for the latter with an additional stacking layer of BO<sub>6</sub> octahedra separating AO (rock salt) layers. The Pm-3m phase acts a reservoir of cations facilitating the formation of an expanded I4/mmm phase structure, while oxygen atoms are sourced from the CO<sub>2</sub> splitting. In addition, the presence of the pyrochlore Ce<sub>2.6</sub>La<sub>1.4</sub>O<sub>6.28</sub> (Fd-3m) minor phase seems to lead to a synergistic interaction with the main perovskite phase (R-3c) of the LSC25M75 composite by contributing to the formation of the *I4/mmm* major phase at high temperatures, thus enhancing the CO<sub>2</sub> splitting ability of the material.

While the synthesis of such promising Ce-substituted perovskite oxides with phase purity and stability both at room temperature as well as under in situ high temperature reaction conditions (i.e., under varying oxygen chemical potentials) remains a challenge, our study highlights that composite materials also demonstrate a promising performance. To this end, long term reactivity and stability testing experiments in an IR-furnace reactor demonstrated that the LSC25M75 composite exhibits about two times higher average CO<sub>2</sub> conversion extent with 142  $\pm$  4 µmoles CO/0.01 mol sample (molar CO<sub>2</sub>:CO = 706:1) compared to pure LSM with 72  $\pm$  4 µmoles CO/0.01 mol sample (molar CO<sub>2</sub>:CO = 1285:1) during the re-oxidation step when tested over 100 thermochemical redox cycles. The detailed structural elucidation of novel Ce-substituted perovskite oxides at in situ high temperature reaction conditions and their enhanced CO<sub>2</sub> splitting performance opens up new avenues of research on Ce-substituted lanthanum strontium manganite-based composites as a promising and tunable class of redox materials for thermochemical fuel production.

## 4. Experimental Section

Synthesis: Initially, six different samples of the initial compositional range La<sup>3+</sup><sub>0.60-x</sub>Sr<sup>2+</sup><sub>0.40+x</sub>Ce<sup>4+</sup><sub>y</sub>Mn<sup>3+</sup><sub>1-y</sub>O<sub>3- $\delta$ </sub> (with y = 0, 0.10, 0.25, 0.40, 0.60, and 1, and x = 2y); labelled as LSM, LSC10M90, LSC25M75, LSC40M60, LSC60M40, and LSC, respectively, were synthesized (2 g scale). A citric acid auto-combustion (citrate sol-gel) method<sup>[52]</sup> was used with the goal of substituting Mn with Ce at the B-site of the perovskite lattice. Stoichiometric quantities of metal nitrate precursors, La(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O (99%), Sr(NO<sub>3</sub>)<sub>2</sub> (99%), Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99%), Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (98%), and citric acid (anhydrous) with a molar ratio of 2:3 were dissolved in 50 mL of deionized water. All chemicals were purchased from Sigma-Aldrich (unless otherwise specified). The sol mixtures were heated at 100-120 °C under continuous stirring, resulting in the formation of a gel due to evaporation of water and decomposition of nitrate precursors. The gel mixtures were left to age overnight to enhance polycondensation and then dried at 400 °C in an oven for 2 h. The organic components in the gel underwent combustion, resulting in a fluffy porous mass. The samples were then ground and transferred to alumina crucibles before calcination at high temperatures. The calcination of samples was performed in air using a 3-step temperature program according to the Tammann rule,<sup>[53]</sup> in order to avoid loss of Mn at high temperatures. The first two steps involve heating at 800 °C (2  $\times$  10 h) which allows perovskite phase formation and a final step at 1300 °C (1  $\times$  20 h) at a ramp rate of 5 °C min<sup>-1</sup> to enable crystal growth and to increase the solubility of dopants through optimal diffusion during the solid-state reaction.<sup>[54]</sup> The repeated heating-up and cooling-down steps result in several melting and re-crystallization cycles of phases in the perovskite composite, thereby maximizing the Ce dopant solubility. Finally, the obtained perovskite oxide powders were ground and sintered at 1350 °C for 4 h at a ramp rate of 5 °C min<sup>-1</sup>

*Characterization*: PXRD measurements of all samples were performed on a Rigaku SmartLab diffractometer with Cu K<sub>al</sub> radiation (8.04 keV/1.5406 Å) in Bragg-Brentano geometry. Cu K<sub>β</sub> radiation was removed with a Ni-filter.

Synchrotron X-ray powder diffraction measurements were carried out at the Material Science beamline (MS-X04SA) at the Swiss light source of the Paul Scherrer Institute, Switzerland. The measurements were conducted at room temperature using a photon energy of 25 keV ( $\lambda = 0.49297$  Å). Samples were loaded in 0.2 mm capillaries and data was collected (step size = 0.0036°) in transmission mode using a Mythen II detector. The exact wavelength and instrument resolution parameters were determined from LaB<sub>6</sub> powder (NIST) and Si standard (Si 640d) sample measurements recorded under identical conditions.

Neutron diffraction experiments were carried out on the high-resolution D2B neutron diffractometer at the Institut Laue-Langevin (ILL, Grenoble, France) using a monochromatic neutron beam with a wavelength of  $\lambda = 1.594$  Å. In situ high-temperature neutron powder diffraction experiments were performed using a standard niobium furnace operated under vacuum conditions ( $10^{-4} - 10^{-3}$  mbar) and data



was recorded at three different temperatures, 25 °C (RT, fresh), 1350 °C, 1000 °C, and a repeated measurement at 25 °C (RT, after cooling). About 2 g of the sample were loaded in niobium sample containers for measuring in situ high-temperature data, whereas vanadium sample containers were used for measuring room temperature neutron diffraction data. The temperature program was intended to mimic the operating conditions of a two-step solar thermochemical fuel production process. Initially, the metal oxide sample was reduced at high temperature (1350 °C) under vacuum ( $p_{O2} \le 10^{-3}$  mbar) conditions, thereby generating oxygen vacancies, followed by cooling down the furnace under vacuum to a re-oxidation temperature at 1000 °C. A heating and cooling ramp rate of 10 °C min<sup>-1</sup> was used to reach target temperatures, followed by a dwell time (isothermal heating) of 1 h to allow the perovskite oxide samples to reach thermal equilibrium before recording data. The counting time for collecting each pattern was 5–6 h.

Rietveld structural refinement of data was performed using the FullProf Suite software.<sup>[55]</sup> The peak profiles were modelled using a pseudo-Voigt function. Scale factor, atomic positions, occupancies, isotropic (synchrotron XRD), and anisotropic (neutron diffraction) atomic displacement parameters at different temperatures were refined. BVS calculations were carried out to estimate the valence (oxidation state) of atoms and further to validate the correctness of the structural model.<sup>[56,57]</sup>

High-resolution scanning transmission electron microscopy, HAADF-STEM images and STEM-EDS elemental maps and analysis were obtained using a FEI Titan Themis (300 kV) equipped with a hexapole-type aberration corrector for a scanning transmission electron microscope (CEOS DCOR) and a super EDX system. The surface morphology and microstructure were characterized by means of field-emission scanning electron microscopy using a Zeiss Supra 50 VP instrument.

Thermogravimetric Redox Cycling Experiments: TGA redox cycling experiments were carried out on a Netzsch STA 449 F3 Jupiter thermal analyzer. About 100 mg of the powder sample were loaded in a shortened alumina crucible Netzsch 3.4 mL GB445213 (cut 12 mm from the top to increase the sample surface exposure to gases). The gas atmospheres and flow rates of Ar (99.999%) and CO<sub>2</sub> (99.995%) were controlled by an electronic mass flow controller. Blank measurement runs were conducted using an empty alumina crucible under the same experimental testing conditions and subtracted from sample measurements to account for buoyancy effects. Initial TGA redox cycling experimental tests were conducted at two different reduction temperatures (1300 and 1350 °C) and three different oxidation temperatures (800, 900, and 1000 °C). During the reduction step of each cycle a gas flow rate of 200 mL min<sup>-1</sup> Ar  $(p_{O2} \approx 10^{-5} \text{ atm})$  was used for the duration of 60 min and for the oxidation step a mixture of 50 mL min<sup>-1</sup> CO<sub>2</sub> and 150 mL min<sup>-1</sup> Ar was used for the duration of 80 min. All volumes reported in this work are at standard conditions, that is, 25  $^\circ$ C and 1 bar. The CO<sub>2</sub> reduction step was started 10 min after the sample cooled down to the desired oxidation temperature. Samples were cooled down under high Ar gas flow rate (200 mL min<sup>-1</sup>) after finishing the redox cycling experiments.

Infrared-Furnace Reactor Redox Cycling Experiments: An infrared (IR) furnace setup reactor was used to test redox cyclability and long-term stability of the newly synthesized perovskite oxide materials for two-step CO<sub>2</sub> splitting cycles. The schematic experimental set-up used is shown in Figure S18, Supporting Information.<sup>[7,8]</sup> The IR-furnace (VHT-E48, Ulvac-Riko, 24 kW power requirement) consists of 4 electric heating elements surrounded by gold-coated water-cooled mirrors reflecting the infrared radiation toward a quartz tube (24 mm outer diameter, 1.5 mm thickness, 500 mm-length) running along the centerline of the furnace. An alumina ceramic crucible containing the powder sample was loaded inside the quartz tube between layers of quartz wool. The inner guartz tube was sealed and surrounded by a second guartz tube (50 mm outer diameter, 45 mm thickness, 360 mm length) to protect the heating elements and the reflective surfaces from damage. The heating length of the furnace was around 230 mm and sample was placed at the center of the furnace. Sample temperature was measured using a B-type thermocouple, which was also used as the control for the Temperature Program Controller (TPC-5000). In addition to the cooling water circulation, cold compressed air was blown onto the IR-furnace heating elements and the outer quartz tube to avoid overheating. The gas flow rates of Ar (99.998%), CO2 (99.995%), and synthetic air were controlled by electronic mass flow controllers (Bronkhorst, EL-FLOW). The LabView (National Instruments) software platform was used to operate electronic mass flow controllers and actuated valves (Swagelok) along with program automation and data acquisition, thus controlling desired gas flow rates in "mL min<sup>-1</sup>." A pressure sensor (PSE54, SMC) measured the differential pressure of the reaction gas stream at the exit of the furnace. The product gas leaving the inner quartz tube was continuously analyzed using a Siemens Ultramat 23 gas analyzer. The Ultramat 23 used herein was equipped with a 3-component gas analyzer, comprising of an electrochemical  $O_2$  sensor (0-5 vol%) and two IR-active gas detectors for CO (0-2 vol%) and CO<sub>2</sub> (20-100 vol%). The gas analyzer components were calibrated using specific calibration gas compositions. The redox cycling experiments were started by heating up the powder sample (8 mmol,  $\approx 2$  g) to a desired reduction temperature  $(T_{\rm red} = 1350 \,^{\circ}{\rm C})$  at a heating rate of 200  $^{\circ}{\rm C}$  min<sup>-1</sup> while flowing Ar gas at a rate  $V_{Ar} = 0.5$  L min<sup>-1</sup>. The sample reduction was continued isothermally at T<sub>red</sub> for 3 min. The reduced metal oxide was then cooled down to the oxidation temperatures ( $T_{oxi} = 800 \,^{\circ}C$ ) at a cooling rate of 200  $^{\circ}$ C min<sup>-1</sup>. The oxidation reaction was carried out isothermally at  $T_{\text{oxi}}$  for 4.5 min by flowing pure CO<sub>2</sub> gas at a rate  $V_{\text{CO2}} = 0.5$  L min<sup>-1</sup>. The samples were pre-oxidized before redox cycling experiments using synthetic air (0.5 L min<sup>-1</sup>) at 1000 °C for 5 min, to ensure complete oxidation and provide relative starting conditions for each sample. The outlet gas concentration was continuously recorded during the redox cycling experiments. The gas concentrations obtained in vol% were then converted and normalized to  $\mu$ moles/0.01 mol of oxide sample.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## **Data Availability Statement**

The data that support the findings of this study are openly available at https://doi.ill.fr/10.5291/ILL-DATA.DIR-181.

### **Keywords**

Ce-perovskite oxides,  $\rm CO_2$  splitting, in situ high temperature neutron diffraction, reaction mechanism, solar thermochemical fuels

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