

## PAPER

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2023, 16, 2550Multiple and nonlocal cation redox in  
Ca–Ce–Ti–Mn oxide perovskites for solar  
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Modeling-driven design of redox-active off-stoichiometric oxides for solar thermochemical H<sub>2</sub> production (STCH) seldom has resulted in empirical demonstration of competitive materials. We report the theoretical prediction and experimental evidence that the perovskite Ca<sub>2/3</sub>Ce<sub>1/3</sub>Ti<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>3</sub> is synthesizable with high phase purity, stable, and has desirable redox thermodynamics for STCH, with a predicted average neutral oxygen vacancy (V<sub>O</sub>) formation energy,  $E_v = 3.30$  eV. Flow reactor experiments suggest potentially comparable or greater H<sub>2</sub> production capacity than recent promising Sr–La–Mn–Al and Ba–Ce–Mn metal oxide perovskites. Utilizing quantum-based modeling of a solid solution on both A and B sub-lattices, we predict the impact of nearest-neighbor composition on  $E_v$  and determine that A-site Ce<sup>4+</sup> reduction dominates the redox-activity of Ca<sub>2/3</sub>Ce<sub>1/3</sub>Ti<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>3</sub>. X-ray absorption spectroscopy measurements provide evidence that supports these predictions and reversible Ce<sup>4+</sup>-to-Ce<sup>3+</sup> reduction. Our models predict that Ce<sup>4+</sup> reduces even when it is not nearest-neighbor to the V<sub>O</sub>, suggesting that refinement of Ce stoichiometry has the possibility of further enhancing performance.

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## Broader context

Sunlight is an abundant albeit low areal density source of renewable energy. Collecting and concentrating the sun's rays for its heat value can enable high-temperature endothermic reactions such as water splitting to produce clean hydrogen. Two-step thermochemical cycles with redox-active metal oxides are promising. However, technoeconomic analyses with state-of-the-art CeO<sub>2</sub> suggest that without a new active material, achieving the US Department of Energy's Hydrogen Shot \$1 per kg H<sub>2</sub> target is unlikely. Here, we introduce a previously unknown material predicted from theoretical considerations and experimentally validated. The material is a redox-active quinary oxide perovskite, CCTM, with solid solutions of Ca/Ce and Ti/Mn on the A- and B-sites, respectively. CCTM offers promising oxygen vacancy thermodynamics and exceptional H<sub>2</sub> yield, when reduced at moderate temperatures and cycled at relatively short reoxidation periods. Modeling reveals and experiment confirms that Ce<sup>4+</sup> is the primary redox-active species, in contrast to other known reducible perovskites, where in all cases the active element sits on the B-site. Furthermore, even with B-site Ce<sup>4+</sup>, that element is not redox active. Hence this work reports the first perovskite with reducible A-site and reducible Ce<sup>4+</sup>, predicted entirely from theory, and subsequently validated with experiments that establish stability, reversibility, and high productivity.

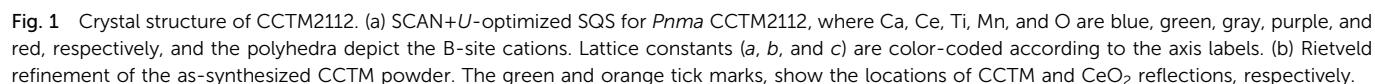
<sup>a</sup> Department of Mechanical and Aerospace Engineering and the Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08544-5263, USA. E-mail: eac@princeton.edu<sup>b</sup> Department of Materials Engineering, Indian Institute of Science, Bengaluru, Karnataka 560012, India<sup>c</sup> National Renewable Energy Laboratory, Golden, CO 80401, USA<sup>d</sup> SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA<sup>e</sup> Sandia National Laboratories, Livermore, CA 94550, USA<sup>f</sup> University of California Santa Cruz, Santa Cruz, CA 95064, USA<sup>g</sup> ASU LightWorks<sup>®</sup> and the School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287-8204, USA. E-mail: ellen.stechel@asu.edu† Electronic supplementary information (ESI) available: Further details about the SCAN+U calculations, stability of CCTM2112, SQS construction for *Pnma* CCTM2112, V<sub>O</sub> NN environment statistics, magnetic moment distribution by species in pristine CCTM2112, dependence of the V<sub>O</sub>-induced magnetic moment changes by element on the V<sub>O</sub>'s NN environment, qualitative Ce and Mn oxidation state changes upon V<sub>O</sub> formation, V<sub>O</sub>-induced magnetic moment changes vs. distance, and projected density of states of pristine CCTM2112;<sup>40–47</sup> additional synthesis details, comparison of H<sub>2</sub> produced by state-of-the-art redox-active perovskites, and XRD and XAS data from the reduced and re-oxidized CCTM powder; files containing crystal structures, total energies, magnetic moments, and projected densities of states. See DOI: <https://doi.org/10.1039/d3ee00234a>

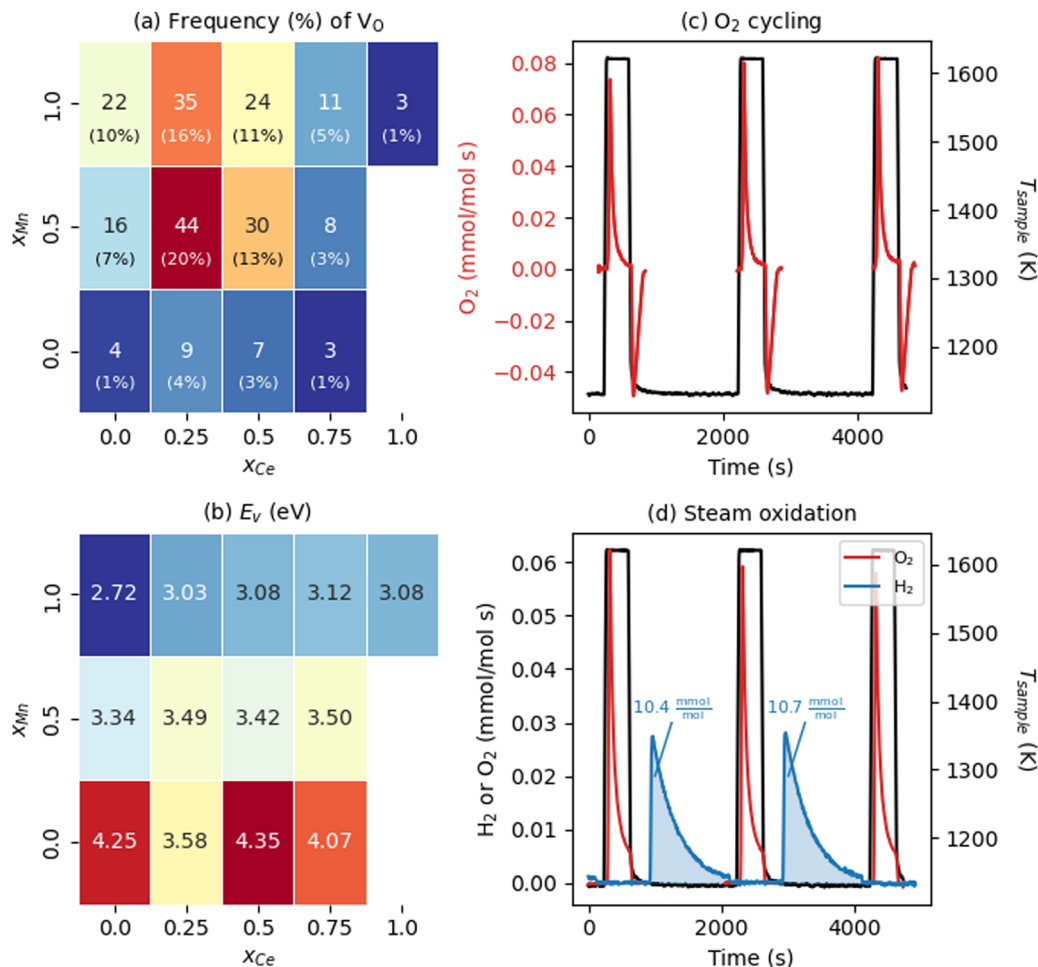
Increasing the  $\eta$  of metal-oxide-perovskite-based STCH toward that of the ideal Carnot cycle generally amounts to

## Results

As is the convention in computational materials science, we quantify stability as the energy above the convex hull ( $E_{\text{hull}}$ ), which is the energy change upon decomposition of a material into stable compounds at the same composition. Throughout, we performed density functional theory (DFT) calculations within the SCAN<sup>21</sup>+ $U$ <sup>22–25</sup> framework (see Section S1 and S2 in the ESI† for additional details regarding the SCAN+ $U$  calculations and  $E_{\text{hull}}$  computation, respectively).<sup>26,27</sup> Based on this convex hull construction, CCM is thermodynamically metastable, with an  $E_{\text{hull}} = 39$  meV per atom at 0 K. Experimental attempts to synthesize CCM perovskite were unsuccessful, with CeO<sub>2</sub> and Ca–Mn oxide phases predominating, and limited Ca–Ce–Mn oxide phase fraction decomposing during even gentle reduction (see Section S3 in the ESI†). We then tried to increase the stability by using the naturally abundant and highly stable CaTiO<sub>3</sub> perovskite as a template to then add a solid solution of Ce<sup>4+</sup> and Mn<sup>3+</sup> on the A- and B-sites, respectively. Beginning with the previously predicted CCM, we increased the fraction of Ca on the A-site (from 1/2 to 2/3) and Ti on the B-sites (from 0 to 1/3). The resulting structure is a *Pnma* Ca<sub>2/3</sub>Ce<sub>1/3</sub>Ti<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>3</sub> solid solution (CCTM2112, where the numbers indicate the relative composition of the material for three formula units or numerators of the fractional A- and B-site compositions for one formula unit), matching the *Pnma* structure of CaTiO<sub>3</sub>. For a preliminary check on stability, we used the  $\tau$  tolerance factor of Bartel *et al.*<sup>28</sup> to predict whether CCTM2112 would form a perovskite. The  $\tau$  value is 2.74, which gives a probability that the composition forms a perovskite structure of 94%, hence, high confidence. Additional support for this solid-solution approach came from reports of CaTi<sub>0.5</sub>–Mn<sub>0.5</sub>O<sub>3– $\delta$</sub> <sup>29</sup> and CaTi<sub>0.2</sub>Mn<sub>0.8</sub>O<sub>3– $\delta$</sub> ,<sup>30</sup> though, in our work, the A-site addition of Ce changes the predominant oxidation state of Mn in the fully-oxidized material from Mn<sup>4+</sup> in the prior purely Ca-A-site perovskites to Mn<sup>3+</sup> in CCTM2112 (see the section entitled Role of Ce<sup>4+</sup> in Redox Activity). Independent simulation and empirical determination of the CCTM2112 crystal structure resulted in strong agreement in lattice parameters and atomic positions.

We now examine the energetics of  $V_O$  formation in CCTM2112 and its dependence on the  $V_O$ 's nearest neighbors (NNs). Inspired by our recent finding that local chemistry governs  $V_O$  formation in ternary metal-oxide perovskites,<sup>36</sup> we categorized all 216  $V_O$ s by their (NN) environment and randomly sampled one  $V_O$  (*i.e.*, we introduce one  $V_O$  in the SQS, corresponding to  $\delta = 0.014$ ) from each of the 13 unique  $V_O$  NN environments (Fig. 2(a)). This categorization also gave a tractable number of SCAN+ $U$  calculations from which to study the trends in the electronic and thermochemical properties of  $V_O$ s. We define NN  $V_O$  environments using  $x_{Ce}$  and  $x_{Mn}$ , where  $x_{Ce} = N_{Ce}/(N_{Ca} + N_{Ce})$ ,  $x_{Mn} = N_{Mn}/(N_{Ti} + N_{Mn})$ , and  $x(N)$  is the fraction (number) of the  $V_O$ 's four NN A-sites and two NN B-sites occupied by Ce ( $x_{Ce} = 1 - x_{Ca}$  and  $N_{Ce} = 4 - N_{Ca}$ ) and Mn ( $x_{Mn} = 1 - x_{Ti}$  and  $N_{Mn} = 2 - N_{Ti}$ ), respectively. Note that the overall supercell structure maintains the same cation stoichiometry as that of bulk CCTM2112, with  $x_{Ce}$  and  $x_{Mn}$  in Fig. 2(a) strictly defining compositions that are local to the  $V_O$  considered. Predictably, the  $V_O$  with the highest frequency ( $f = 44$  or  $44/216 \approx 20\%$  of the SQS) is the one with a NN environment





**Fig. 2** Water-splitting properties of CCTM2112. (a) Frequency (color of and text in rectangles) and probability (percentages in parentheses rounded to the nearest integer) of all unique NN  $V_O$  environments in the calculated CCTM2112 360-atom cell (and, in Table S6, ESI† for the random alloy), with dark red and dark blue shading indicating higher- and lower-frequency environments, respectively. (b) NN- $V_O$ -environment dependence of calculated  $E_v$  in CCTM2112. Color of and text in rectangles correspond to  $E_v$  in eV, where the minimum  $E_v = 2.72$  eV is dark blue and maximum  $E_v = 4.35$  eV is dark red. (c)  $O_2$  evolution rate normalized to mole atoms in CCTM2112 (see ESI†, Section S5 for definition) measured as a function of time during heating and cooling between 1123 K and 1623 K in a constant background of 2000 ppm oxygen. (d)  $O_2$  and  $H_2$  evolution rates normalized to mole atoms in CCTM2112 measured as a function of time during two successive redox cycles where the sample temperature is raised to 1623.15 K while sweeping with high purity Ar, followed by exposure to 40 vol%  $H_2O$  in Ar at 1123.15 K. The area under the gas evolution features in (c) and (d) is used to quantify the redox capacity of CCTM2112 during oxygen and steam oxidation.

closest to the bulk composition allowed by the A and B site NN fractions ( $x_{Ce} = 0.25$  and  $x_{Mn} = 0.5$  for the  $V_O$  and  $x_{Ce} = 1/3$  and  $x_{Mn} = 2/3$  for the bulk). Two NN  $V_O$  environments do not appear in the optimized SQS for CCTM2112 (namely those for  $x_{Ce} = 1$  and  $x_{Mn} \leq 0.5$ ), however,  $V_O$ s with these NN environments are unlikely to influence significantly the macroscopic reduction of CCTM2112 due to their scarcity ( $x_{Ce} = 1$  and  $x_{Mn} = 0.5$ , and  $x_{Ce} = 1$  and  $x_{Mn} = 0$  make up 0.5% and 0.1% of the random alloy, respectively).

With this  $V_O$  categorization protocol, we predict that five of the 13  $V_O$ s (shaded yellow and light blue in Fig. 2(b)), including those with the first- and third-highest frequencies ( $f = 44$  or  $44/216 \approx 20\%$  for  $x_{Ce} = 0.25$  and  $x_{Mn} = 0.5$ , which is 17.6% in a random solid (Table S6, ESI†), and  $f = 30$  or  $30/216 \approx 14\%$  for  $x_{Ce} = x_{Mn} = 0.5$ , which is 13.2% of the sites in a random solid), have  $E_v$ s within (or within 0.06 eV of) the target range of 3.4–3.9 eV (see Fig. 2(b)).<sup>19</sup> To quantify the macroscopic reducibility

of CCTM2112, we calculate the ensemble-averaged  $E_v$ ,  $\langle E_v \rangle = \sum_i f_i E_{v,i} / \sum_i f_i$ , where  $f_i$  is the frequency of the  $i^{th}$  unique NN  $V_O$  environment given in Fig. 2(a), and  $\sum_i f_i = 216$ . We obtain  $\langle E_v \rangle = 3.30$  eV with a standard deviation of 0.36 eV based on the  $E_v$  values in Fig. 2(b), which overlaps with the target range for water splitting. We find that while  $E_v$  depends weakly on  $x_{Ce}$ , it systematically decreases with increasing  $x_{Mn}$ . This trend can be rationalized on the basis of crystal  $O^{2-}-M^{n+}$  bond dissociation energies  $E_b$ , an extension of molecular O–M bond dissociation energies to the solid state,<sup>36</sup> defined as

$$E_b[O^{2-} - M^{n+}] = \frac{E_c[MO_{n/2}]}{N_b[O^{2-} - M^{n+}]} \quad (1)$$

where  $n$  is the oxidation state of the metal cation (M),  $E_c[MO_{n/2}]$

is the cohesive energy of the ground-state polymorph of the binary metal-oxide crystal  $\text{MO}_{n/2}$  containing  $\text{M}^{n+}$ , and  $N_{\text{b}}[\text{O}^{2-}-\text{M}^{n+}]$  is the number of  $\text{O}^{2-}-\text{M}^{n+}$  bonds per  $\text{MO}_{n/2}$  formula unit. In short,  $E_{\text{v}} \propto -x_{\text{Mn}}$  because  $\text{O}^{2-}-\text{Mn}^{4+}$  (crystal bond dissociation energy  $E_{\text{b}} = 2.25$  eV) and  $\text{O}^{2-}-\text{Mn}^{3+}$  (1.97 eV) crystal bonds are weaker than  $\text{O}^{2-}-\text{Ti}^{4+}$  (3.16 eV) and  $\text{O}^{2-}-\text{Ti}^{3+}$  (2.62 eV).<sup>36</sup>

Experiments demonstrate that CCTM2112 is a high-performance water splitter. The data presented in Fig. 2(c) and (d) were measured in a stagnation flow reactor dedicated to screening STCH materials.<sup>16,17</sup> During dry redox cycling with  $\text{O}_2$  (Fig. 2(c)) the material is continuously exposed to  $\approx 2000$  ppm  $\text{O}_2$  while heating from a base temperature of 1123 K to 1623 K. During heating (*i.e.*, thermal reduction) the material evolves molecular oxygen as  $\text{V}_{\text{O}}$ s form in the crystal lattice, hence the positive rate of  $\text{O}_2$  production. Upon cooling to 1123 K, the material uptakes an equivalent amount of  $\text{O}_2$  from its surroundings as the  $\text{V}_{\text{O}}$ s are refilled, hence the negative rate of production. CCTM2112 is also redox active under the more stringent thermodynamic conditions of water splitting, as evidenced in Fig. 2(d). Here the sample is exposed to a high purity Ar sweep gas during thermal reduction followed by exposure to a mixture of 40 vol%  $\text{H}_2\text{O}$  in Ar. As with  $\text{O}_2$  redox, molecular oxygen is produced by thermal reduction. However, in the water splitting case, O atoms stripped from  $\text{H}_2\text{O}$  fill  $\text{V}_{\text{O}}$ s such that  $\text{H}_2$  evolves in the presence of steam. Finally, when reduced a second and third time (after steam re-oxidation), an equivalent amount of  $\text{O}_2$  evolves from the material at levels indicative of the first cycle. The  $\delta$  calculated from the oxygen reduction in the flow reactor is  $\delta = 0.06$ , with the cycling  $\Delta\delta = 0.05$ . Due to different operating regimes, this  $\delta$  for the flow reactor is approximately twice that of the soft XAS ( $\delta = 0.033$ , *vide infra*) and four times the modeling conditions (one vacancy per 360 atom structure or  $\delta = 0.014$ , *vide supra*). The data in Fig. 2(d) demonstrates that CCTM2112 is reversibly redox active (for several cycles) in both  $\text{O}_2$  and  $\text{H}_2\text{O}$ . Furthermore, the absolute amount of  $\text{O}_2$  and  $\text{H}_2$  produced during 40 vol% steam cycling (area under blue curve = 10.4 mmol  $\text{H}_2$  per mol atom CCTM2112) exceeds that of other high-performing perovskite compounds such as  $\text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3$  (7.3 mmol  $\text{H}_2$  per mol atom BCM) and  $\text{Sr}_{0.4}\text{La}_{0.6}\text{Mn}_{0.6}\text{Al}_{0.4}\text{O}_3$  (8.2 mmol  $\text{H}_2$  per mol atom SLMA), and  $\text{CeO}_2$  (2.9 mmol  $\text{H}_2$  per mol atom  $\text{CeO}_2$ ) under similar experimental conditions (see Section S5 in the ESI† for the calculation of the  $\text{H}_2$  produced by these perovskite compounds). Note that  $\text{CeO}_2$  does poorly under these conditions, *e.g.*, compared with thermal reduction at  $\approx 1800$  K.<sup>8</sup> In future work, we will pursue a more thorough comparison between all of these materials in the context of “high conversion,” which is re-oxidation in a less oxidizing environment, such as 1:1000  $\text{H}_2:\text{H}_2\text{O}$  in the oxidizing stream. Normalizing to mole atom (see ESI† Section S5 for definition) makes these comparisons possible, without biasing one material over another.

### Role of $\text{Ce}^{4+}$ in redox activity

We aim to develop a mechanistic understanding of the high performance of CCTM2112 compared to the structurally related CTM and the Ce- and Mn-containing BCM perovskite water splitters. We therefore calculated and analyzed atomic magnetic

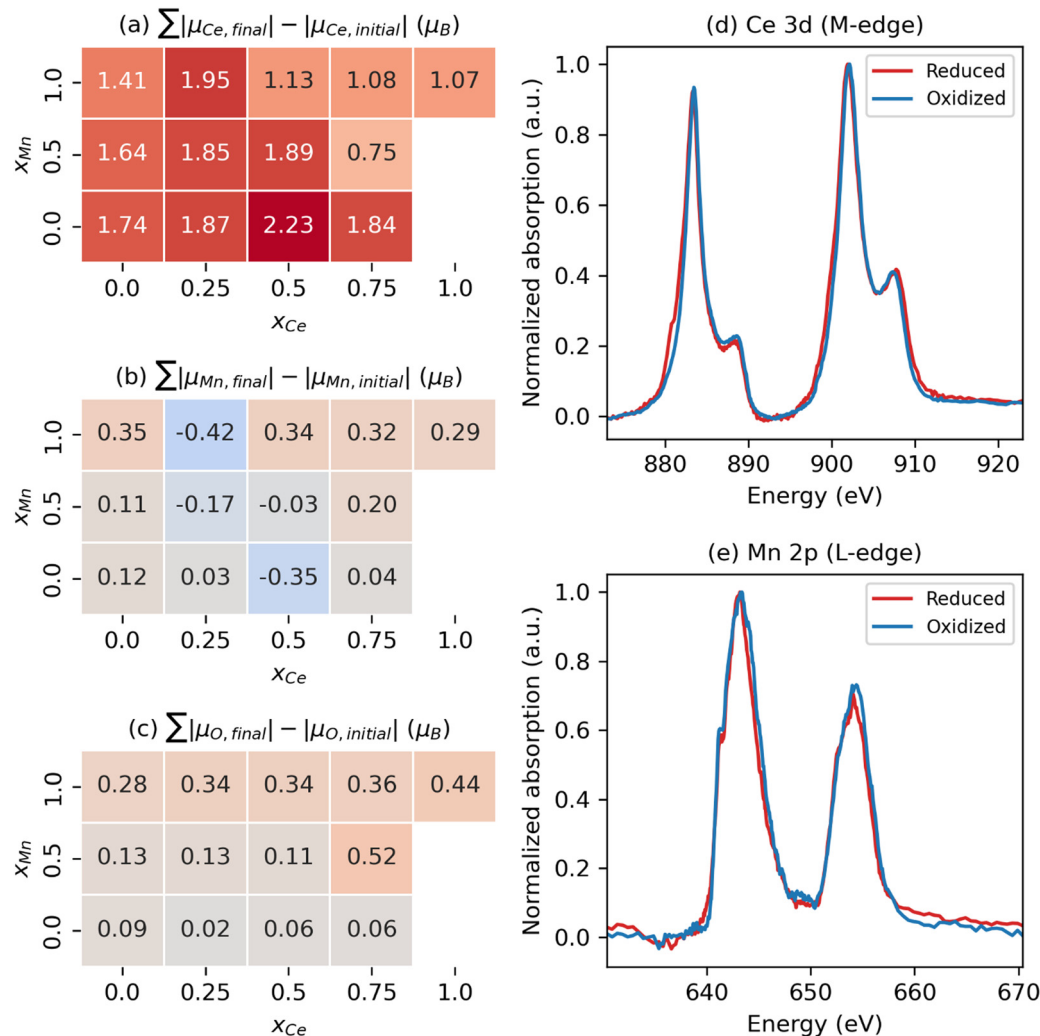
moments ( $\mu$ ), which are extremely sensitive measures of oxidation- and spin-state changes. For fully oxidized CCTM2112, the mean magnetic moments in Table 1 imply that, rounded to the nearest integer, the average oxidation states of Ca, Ce, Ti, Mn, and O are 2+, 4+, 4+, 3+, and 2−, respectively, which leads to a charge neutral formula unit (see Fig. S4 in the ESI† for the  $\mu$  distributions). That said, Ce also can exist as  $\text{Ce}^{3+}$  and Mn as  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$  (see min/max values in Table 1), where the latter suggests that disproportionation of two  $\text{Mn}^{3+}$  may occur in pristine CCTM2112.

To gain greater insight into the nature of the electronic reorganization in CCTM2112 upon  $\text{V}_{\text{O}}$  formation in the thermal reduction step of STCH, we computed the  $\text{V}_{\text{O}}$ -induced changes in the absolute values of  $\mu_{\text{Ce}}$ ,  $\mu_{\text{Mn}}$ , and  $\mu_{\text{O}}$  (use of absolute values controls for changes in relative orientation, *i.e.*, ferromagnetic or antiferromagnetic; see Fig. S5 in the ESI† for a similar analysis of  $\mu_{\text{Ca}}$  and  $\mu_{\text{Ti}}$ ). We then sum these  $|\mu|$  changes separately for Ce, Mn, and O to quantify the extent to which the A, B, and O sub-lattices, respectively, are reduced (positive value) or oxidized (negative value) since changes in  $\mu$  roughly correspond to changes in oxidation states, excluding Ca and Ti because we observe no more than marginal spin changes on these sites. Thus, the quantification of number of electrons added/removed from a species comes from our calculated changes in  $|\mu|$ . For example, when  $x_{\text{Ce}} = 0$  and the change in  $|\mu_{\text{Ce}}| \neq 0$ , a  $\text{V}_{\text{O}}$  without a NN Ce has reduced a non-NN Ce, thus resulting in nonlocal or delocalized reduction.

Our results show that reduction occurs primarily on the A-site Ce sub-lattice (Fig. 3(a)) compared with that of Mn (Fig. 3(b)) and O (Fig. 3(c)), regardless of the  $\text{V}_{\text{O}}$ 's NNs. In particular, the Ce sub-lattice reduces by 0.75 to 2.23 electrons depending on  $x_{\text{Ce}}$  and  $x_{\text{Mn}}$ , corresponding to an average decrease in Ce oxidation state of 0.031 to 0.093 e, respectively (average reduction of the 24 Ce in the unit cell); whereas, for Mn, no obvious net reduction or oxidation occurs during the formation of the  $\text{V}_{\text{O}}$ , with both mild reduction ( $\leq 0.35$  electrons accepted) and oxidation ( $\leq 0.42$  electrons donated) of Mn occurring simultaneously (see Table S7 in the ESI† for a qualitative analysis of Ce and Mn oxidation state changes upon neutral  $\text{V}_{\text{O}}$  formation). During  $\text{V}_{\text{O}}$  formation, the remaining O sub-lattice experiences weak-to-mild reduction ( $\leq 0.52$  electrons accepted in total by the O sub-lattice containing 216 atoms in the unit cell), reminiscent of the  $\text{V}_{\text{O}}$ -induced delocalized reduction of the O sub-lattice in the  $\text{Sr}_2\text{Fe}_{2-x}\text{Mo}_x\text{O}_6$  double perovskites reported by Muñoz-García *et al.*<sup>37</sup> The reduction of the O sub-lattice is indicative of empty O states in the pristine material,

**Table 1** Magnetic moment summary statistics for fully oxidized CCTM2112.  $\sigma$  is the first standard deviation. All values are in  $\mu_{\text{B}}$ . Fig. S4 in the ESI shows the magnetic moment distributions

Element	Mean $\pm \sigma$	Minimum	Maximum
Ca	0.00 $\pm$ 0.00 ( $\text{Ca}^{2+}$ )	0.00 ( $\text{Ca}^{2+}$ )	0.00 ( $\text{Ca}^{2+}$ )
Ce	0.28 $\pm$ 0.23 ( $\text{Ce}^{4+}$ )	0.06 ( $\text{Ce}^{4+}$ )	0.68 ( $\text{Ce}^{3+}$ )
Ti	0.05 $\pm$ 0.02 ( $\text{Ti}^{4+}$ )	0.03 ( $\text{Ti}^{4+}$ )	0.08 ( $\text{Ti}^{4+}$ )
Mn	3.77 $\pm$ 0.24 ( $\text{Mn}^{3+}$ )	3.10 ( $\text{Mn}^{4+}$ )	4.50 ( $\text{Mn}^{2+}$ )
O	0.01 $\pm$ 0.01 ( $\text{O}^{2-}$ )	0.00 ( $\text{O}^{2-}$ )	0.05 ( $\text{O}^{2-}$ )



**Fig. 3** Multiple cation redox in CCTM2112. Dependence of  $V_O$ -induced absolute magnetic moment ( $|\mu|$ ) changes for the (a) Ce, (b) Mn, and (c) O sub-lattices on the  $V_O$ 's NN environment, where the mole fractions,  $x$ , refer just to the NN environment. Note that we sum these  $|\mu|$  changes separately for Ce, Mn, and O to quantify the extent to which the A, B, and O sub-lattices, respectively, are reduced (positive value) or oxidized (negative value) since  $\mu$  changes roughly correspond to fractional oxidation state changes, reserving Ca and Ti for Fig. S5 in the ESI† because we observe marginal spin changes on these sites. XAS spectra at the (d) Ce 3d<sub>5/2</sub> and (e) Mn 2p<sub>3/2</sub> edge for reduced CCTM2112 and re-oxidized CCTM2112 (see Fig. S8 in the ESI† for the complete spectra).

indicating that the Os are not fully ionized as  $O^{2-}$  (as seen by Bader charge analysis), with instead the M–O bonds exhibiting some singlet-coupled covalent character, which spin-averages the electrons on O to appear nonmagnetic.

X-ray absorption (XAS) synchrotron studies provide validating evidence supporting the predicted changes in average Ce and Mn oxidation states indeed occur during reduction of CCTM2112. We confirmed that, for oxidized CCTM2112 ( $\delta \approx 0$ ), the predominant oxidation states of Mn and Ce are  $Mn^{3+}$  and  $Ce^{4+}$  by comparing the XAS spectrum of oxidized CCTM2112 (Fig. 3(d) and (e)) to standards. CCTM2112 was repeatedly reduced ( $p_{O_2} \approx 1 \times 10^{-5}$  bar) and re-oxidized ( $p_{O_2} \approx 0.2$  bar) in dry redox cycling conditions at 1473 K with 16 hours at each condition. CCTM2112 samples after both the third reduction and third re-oxidation were characterized. XRD confirms both the reduced and re-oxidized sample retained the CCTM structure with negligible secondary

phase formation (Fig. S6, ESI†). Mass change in the sample between re-oxidizing and reducing conditions is consistent with a  $\Delta\delta = 0.033 \pm 0.003$ , with near full oxidation of the re-oxidized sample ( $\delta \approx 0$ ) giving the reduced sample  $\delta = 0.033 \pm 0.003$ . In comparison, the one  $V_O$  out of 216 oxygen sites modeled here (Fig. 2) corresponds to  $\delta = 0.014$ , conditions that are roughly half of the empirical reduction but still sufficiently close for comparing modeling results to observational data.

Soft XAS experiments at the Ce M-edge (*i.e.*, X-ray-induced electron transitions from 3d to 4f orbitals) and Mn L-edge (electron transitions from 2p to 3d orbitals) were used to identify cation-specific changes in oxidation state. Increases in oxidation state result in less electron shielding of the atomic nucleus. Hence, more energy is required to excite a core electron, moving the spectrum edge position to higher energy. Ce and Mn oxidation states were benchmarked against known

standards:  $\text{CeO}_2$  for  $\text{Ce}^{4+}$ ,  $\text{CeAlO}_3$  for  $\text{Ce}^{3+}$ ,  $\text{MnO}_2$  for  $\text{Mn}^{4+}$ ,  $\text{Mn}_2\text{O}_3$  for  $\text{Mn}^{3+}$ , and  $\text{MnO}$  for  $\text{Mn}^{2+}$ . The soft XAS results for the Ce M-edge (see Fig. 3(d)) demonstrate reversible reduction of Ce (shift in edge positions at approximately 881 eV and 900 eV to lower energy upon reduction) to a fractional oxidation state of  $\approx 3.90 \pm 0.03$ , determined from a linear combination fit of the re-oxidized and reduced CCTM with the  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  standards (see Fig. S7 and S8 in the ESI†). This measured 1.1% decrease in the average Ce oxidation state  $[(4 - 3.9)/4 = 2.5\% \text{ for } \delta = 0.033, \approx 2.5 \times 0.014/0.033 = 1.1\% \text{ for } \delta = 0.014]$  agrees well with the 0.8% decrease predicted by SCAN+U calculations  $[(\langle q_{\text{ox}} \rangle - \langle q_{\text{red}} \rangle)/\langle q_{\text{ox}} \rangle = [3.72 - 3.69]/3.72 = 0.8\% \text{ for } \delta = 0.014]$ , where  $\langle q \rangle$  is the ensemble-averaged Ce oxidation state). Additionally, the Mn L-edge (see Fig. 3(e)) demonstrates no observable shift in edge positions (at approximately 641 eV and 652 eV), but does have evidence of  $\text{Mn}^{2+}$  oxidation to  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  reduction to  $\text{Mn}^{3+}$  (loss in intensity at the lower energy shoulder and higher energy side of the spectrum), supporting model predictions that simultaneous Mn oxidation and reduction occurs with modest net change in Mn oxidation state compared with that of Ce (see smaller values with positive and negative signs for Mn in Fig. 3(b) compared with larger positive values for Ce in Fig. 3(a)).

## Discussion

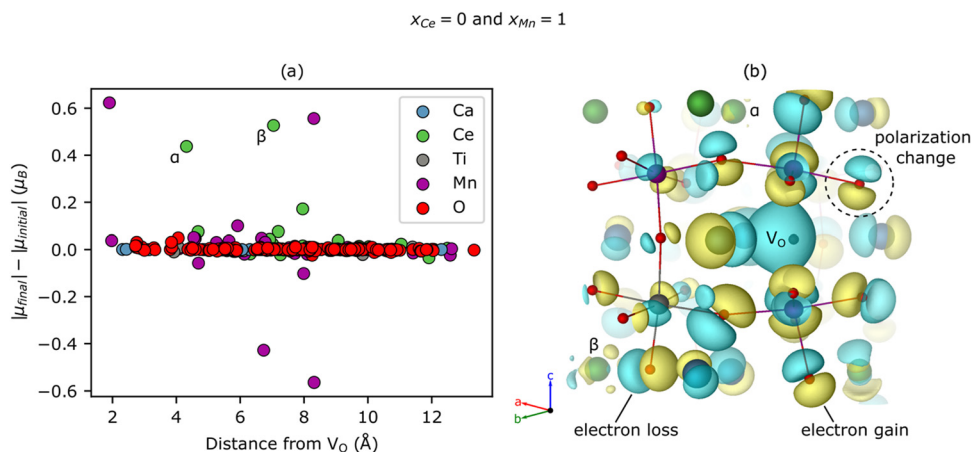
### Nonlocal Ce reduction

Surprisingly, we predict that Ce reduces even when it does not neighbor the  $\text{V}_\text{O}$  (see  $\geq 1.41$  electron reduction of the Ce sub-lattice for  $x_{\text{Ce}} = 0$  in Fig. 3(a)). To explore this phenomenon further, we study the spatial dependence of the  $|\mu|$  changes induced by a  $\text{V}_\text{O}$  with a Ca- and Mn-rich local environment (*i.e.*,  $x_{\text{Ce}} = 0$  and  $x_{\text{Mn}} = 1$ ). Fig. 4(a) shows that two Ce reduce, labeled  $\alpha$  ( $\Delta|\mu| = 0.44 \mu_\text{B}$ ) and  $\beta$  ( $0.53 \mu_\text{B}$ ), at distances of 4.32 Å (for  $\alpha$ ) and 7.04 Å (for  $\beta$ ) from the  $\text{V}_\text{O}$ . Note that Ca and Ti are not redox

active and only a few O are slightly reduced or become more ionic, mostly at distances of  $< 5$  Å from the  $\text{V}_\text{O}$ , which accounts for the non-zero value in Fig. 3(c) for  $x_{\text{Ce}} = 0$  and  $x_{\text{Mn}} = 1$ . Additionally, the Mn sub-lattice is both reduced and – to a slightly lesser extent – oxidized, leading to a net mild reduction of 0.35 electrons, corresponding to a disproportionation. Given the changes for Mn are modest, experimental validation is non-trivial. Ce reduction-at-a-distance also can be seen in Fig. 4(b), which displays the difference between the electron density ( $\rho$ ) of CCTM2112 with and without (*i.e.*, in its pristine state) this same neutral  $\text{V}_\text{O}$  ( $\Delta\rho = \rho_{\text{vacancy}} - \rho_{\text{pristine}}$ ), as yellow isosurfaces (indicating electron gain) emerging from and surrounding the two green Ce labeled  $\alpha$  and  $\beta$ , respectively. There are a lot of cyan isosurfaces as well, which implies, in the cases where  $\Delta\rho$  is p-like polarization rather than charge accumulation or depletion at those sites. This nonlocal reduction allows a substantial fraction of the Ce present in the material to participate in oxygen vacancy formation, and partially explains the high extent of Ce reduction in CCTM2112.

Having explored the spatial dependence of  $\text{V}_\text{O}$ -induced reduction, we now are able to explain the subtle  $x_{\text{Ce}}$  dependence of  $E_\text{v}$  at  $x_{\text{Mn}} = 0$ . The  $E_\text{v}$  for  $x_{\text{Ce}} = 0$  (*i.e.*, 4.25 eV) is the second highest value in Fig. 2(b), which we attribute to the localized reduction of Ce ( $\approx$  two Ce reduced in Fig. S9 of the ESI†), and the electrostatic penalty associated with its distance (4.67–4.83 Å) from the holes localized on the  $\text{V}_\text{O}$  (see, *e.g.*, Fig. 4(b)). For  $x_{\text{Ce}} = 0.25$ , the  $E_\text{v} \approx 3.58$  eV (Fig. 2(b)) is anomalously low because, while the reduction of Ce remains fairly localized (two Ce reduced at distances  $< 5$  Å to the  $\text{V}_\text{O}$ , Fig. S9, ESI†), these electrons are closer to the  $\text{V}_\text{O}$ -generated holes and therefore electrostatically stabilize the  $\text{V}_\text{O}$ . Note that strain can have an indirect effect on  $E_\text{v}$  by inducing or relaxing Jahn–Teller distortions on Mn but the strain effect is difficult to quantify.

Interestingly,  $E_\text{v}$  reaches its highest value for  $x_{\text{Ce}} = 0.5$  (*i.e.*, 4.35 eV; Fig. 2(b)), which we propose is the sum of (1) an electrostatic penalty for delocalized reduction of Ce (four Ce



**Fig. 4** Nonlocal Ce reduction in CCTM2112 upon formation of a  $\text{V}_\text{O}$  in a Ca- and Mn-rich local environment ( $x_{\text{Ce}} = 0$  and  $x_{\text{Mn}} = 1$ ). (a)  $\text{V}_\text{O}$ -induced magnetic moment changes vs. distance, with two Ce ( $\alpha$  and  $\beta$ ) highlighted. (b) Electron density difference upon  $\text{V}_\text{O}$  formation,  $\Delta\rho = \rho_{\text{vacancy}} - \rho_{\text{pristine}}$ , where  $\rho_{\text{vacancy}}$  and  $\rho_{\text{pristine}}$  are the electron densities of CCTM2112 with and without the  $\text{V}_\text{O}$ . Isosurfaces correspond to a  $\Delta\rho$  value of  $0.06 \text{ e } \text{\AA}^{-3}$ , with yellow and cyan isosurfaces corresponding to regions of electron gain and loss, respectively.

Lastly, it is worth discussing an interesting question that our results provoke: why does  $\text{Ce}^{4+}$  function as the primary acceptor of electrons (Fig. 3(a)) if it is less reducible than  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$ ? To quantify the reducibility of  $\text{Ce}^{4+}$ ,  $\text{Mn}^{4+}$ , and  $\text{Mn}^{3+}$ , we calculate the enthalpy changes of the following solid-state reduction reactions:  $\text{CeO}_2 \rightarrow 0.5 \text{ Ce}_2\text{O}_3 + 0.25 \text{ O}_2$ ,  $\text{MnO}_2 \rightarrow 0.5 \text{ Mn}_2\text{O}_3 + 0.25 \text{ O}_2$ , and  $0.5 \text{ Mn}_2\text{O}_3 \rightarrow \text{MnO} + 0.25 \text{ O}_2$ , respectively.  $\text{Mn}^{4+}$  is the most reducible cation ( $\Delta H = 0.40 \text{ eV}$ ) followed by  $\text{Mn}^{3+}$  ( $\Delta H = 1.02 \text{ eV}$ ) and then  $\text{Ce}^{4+}$  ( $\Delta H = 1.82 \text{ eV}$ ). Additionally, since these reactions are normalized per one-electron reduction, their  $\Delta H$ s are effectively crystal reduction potentials ( $V_r$ ), which are a key factor governing  $E_v$  in ternary oxide perovskites.<sup>36</sup> While this simple analysis suggests that Ce should not reduce, the unoccupied states closest to the Fermi level in metallic CCTM2112 are Ce 4f states (see Fig. S10 in the ESI<sup>†</sup>). Therefore, even though  $\text{Ce}^{4+}$  is less reducible than  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  in their ground-state binary oxides, Ce does reduce in CCTM2112 because there is a lower energy penalty for the structure to put the  $\text{V}_\text{O}$ -donated electrons in the Ce 4f states, even if the Ce atom is physically farther from the  $\text{V}_\text{O}$ .  $\text{Ce}^{4+}$  reduction is also accompanied by delocalization of electrons (due to the degeneracy of 4f states contributed by several Ce atoms close to the Fermi level), while Mn reduction is almost always local, evidenced by the presence or absence of Jahn-Teller distortions associated with  $\text{Mn}^{3+}$ . The need for 4f states near the Fermi level to reduce  $\text{Ce}^{4+}$  in the presence of  $\text{Mn}^{3+}$  is consistent with the observation that Mn and not Ce reduces during thermochemical cycling of  $\text{Ba}(\text{Ce},\text{Mn})\text{O}_3$  (BCM) perovskites (where Ba is on the A-site, and Ce and Mn occupy the B-site)<sup>17</sup> because BCM has a band gap and thus  $\text{V}_\text{O}$ -induced reduction is driven by cation proximity and reducibility rather than the relative location of unoccupied states near the Fermi level. Thus, the density of states for CCTM2112 promotes Ce reduction, revealing a mechanism that quantum-based modeling can target to predict other formulations of Ca-Ce-Ti-Mn-O as well as other materials with enhanced Ce reduction and thus enhanced STCH performance.

The high reducibility of  $\text{Ce}^{4+}$  in CCTM2112 is both key to its high water-splitting performance and substantially different than the behavior of  $\text{CeO}_2$  and other previously demonstrated  $\text{Ce}^{4+}$ -containing off-stoichiometric redox-active materials. The existence of  $\text{Ce}^{4+}$  reduction is observed directly in both modeling

and XAS. The most obvious structural distinction of CCTM2112 is the 12-fold coordination of  $\text{Ce}^{4+}$  on the A-site, compared to the 8-fold coordination of  $\text{Ce}^{4+}$  in the  $\text{CeO}_2$  fluorite structure and 6-fold coordination on the B-site of BCM. As discussed above, the redox activity of Mn on the B-site is less clear, which suggests that other electronically similar elements may be able to substitute on the B-site and enable A-site  $\text{Ce}^{4+}$  reduction.<sup>20</sup> These results further suggest that a heretofore under-investigated family of  $\text{Ce}^{4+}$  A-site perovskites may exist with comparably high performance, across a range of alternate A-site and B-site elemental substitutions and ratios.

Perovskite  $\text{Ca}_{2/3}\text{Ce}_{1/3}\text{Ti}_{1/3}\text{Mn}_{2/3}\text{O}_3$  (CCTM2112) offers potential to have greater solar thermochemical  $\text{H}_2$  (STCH) production capacity than two other high-performing perovskite compounds, specifically  $\text{Sr}_{0.4}\text{La}_{0.6}\text{Mn}_{0.6}\text{Al}_{0.4}\text{O}_3$  (SLMA4664) and  $\text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3$  (BCM), and greater than  $\text{CeO}_2$  at operating temperatures of 1623.15 K for the thermal reduction step and 1123.15 K for the water-splitting step. Additionally, the more general Ca–Ce–Ti–Mn–O phase space provides possibilities for supplanting  $\text{CeO}_2$ -based materials as the preferred redox-active  $\text{MO}_x$  for STCH. Ce being the dominant acceptor of the electrons left behind by neutral oxygen vacancy formation, unlike other Ce-containing oxide perovskites for STCH like BCM, suggests that refinement of the Ce stoichiometry is a particularly promising avenue for future research. Finally, the electronic-structure-based mechanism that promotes Ce reduction with lower vacancy formation energies than in  $\text{CeO}_2$  reveals novel physics and redox-active materials design considerations for realizing the climate-change-mitigation potential of STCH. As such, this work does not just introduce one high-performing material but instead uses the modeling-driven and experimentally verified discovery of a new water splitter with a distinct mechanism of action to introduce a new family of water-splitting materials.

Synchrotron powder X-ray diffraction data were acquired at the Stanford Synchrotron Radiation Lightsource (SSRL), beam line 2-1. The incident X-ray wavelength used was 0.730 Å as determined by a refinement of data from a NIST 660C LaB<sub>6</sub> diffraction standard. CCTM powders were prepared in 0.028 inch outer diameter Kapton capillaries with 0.002 inch wall thickness and rotated ( $\approx 1$  rotation per second) during data acquisition. 2D diffraction images were obtained with a Pilatus 100 K hybrid photon counting detector, and subsequently integrated into a 1D pattern using a python script developed at SSRL for beam line 2-1. The diffraction pattern used to compare the experimental XRD data to the DFT model was simulated from the “CCTM2112” model, subjected to the ADDSYM routine within PLATON.<sup>38</sup> The XRD data was indexed using NTREOR, contained

within the EXPO2014<sup>39</sup> suite of crystallographic tools. Rietveld refinements were performed using GSAS-II.<sup>33</sup>

X-Ray absorption spectroscopy data was acquired at SSRL, beam line 10-1. For analysis of each sample, a thin layer of CCTM powder was spread on carbon tape. Total fluorescence yield spectra were obtained with a silicon diode AXUV100 detector at the Ce 3d and Mn 2p edges. A Mn reference spectrum was collected simultaneously with data collection at the Mn edge for all samples. Specific to this beamline, an agglomerate of chemical species resides permanently within the beam path for reference collection. The reference material does not contain Ce, so no Ce reference was available. However, the Mn references collected throughout the experiment well align ensuring the monochromator was stable and data could be directly compared. Data was analyzed with Igor Pro (Wave-metrics, Lake Oswego, Oregon, USA). For each spectrum, the average value of the pre-edge region is subtracted, and the spectrum normalized to the Mn 2p<sub>3/2</sub> or Ce 3d<sub>5/2</sub>. Powder CCTM2112 samples were redox cycled in a laser-heated stagnation flow reactor.<sup>16,17</sup> Approximately 100 mg of sample is placed in a shallow, loosely packed bed within the stagnation plane of the reactor flow field such that transport of gaseous species to and from the sample surface is governed by 1-D diffusion. The reactor operates at 75 Torr and the sample environment (*i.e.*, gas flow rate, gas composition, temperature, pressure) is fully controlled using appropriate hardware and software. The gas composition in the reactor effluent is measured by mass spectrometry at a rate  $\sim 4$  Hz, which is important because the re-oxidation and reduction chemistries are inherently transient. Since the reactor flow field is well behaved, physical processes such as gas-phase dispersion, reactant mixing, and detector time lag that normally confound the extraction of material-specific behavior from the as-measured transient signal are easily resolved using numerical methods. One unique feature of the experimental system is the use of a 500 W, continuous-wave, near-IR laser to rapidly heat the material during thermal reduction. This heating method mimics the radiative environment encountered in an ultra-high temperature concentrating solar receiver and allows exploration of the effects of rapid thermal cycling, such as crystallographic and morphological instabilities, on macroscopic water splitting behavior.

## Conflicts of interest

There are no conflicts to declare.

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