Solar thermochemical hydrogen (STCH) production is a promising method to generate carbon neutral fuels by splitting water utilizing metal oxide materials and concentrated solar energy. The discovery of materials with enhanced water-splitting performance is critical for STCH to play a major role in the emerging renewable energy portfolio. While perovskite materials have been the focus of many recent efforts, materials screening can be time consuming due to the myriad chemical compositions possible. This can be greatly accelerated through computationally screening materials parameters including oxygen vacancy formation energy, phase stability, and electron effective mass. In this work, the perovskite Gd_{0.5}La_{0.5}Co_{0.5}Fe_{0.5}O_{3} (GLCF), was computationally determined to be a potential water splitter, and its activity was experimentally demonstrated. During water splitting tests with a thermal reduction temperature of 1,350°C, hydrogen yields of 101 μmol/g and 141 μmol/g were obtained at re-oxidation temperatures of 850 and 1,000°C, respectively, with increasing production observed during subsequent cycles. This is a significant improvement from similar compounds studied before (La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3} and LaFe_{0.75}Co_{0.25}O_{3}) that suffer from performance degradation with subsequent cycles. Confirmed with high temperature x-ray diffraction (HT-XRD) patterns under inert and oxidizing atmosphere, the GLCF mainly maintained its phase while some decomposition to Gd_{2-x}La_{x}O_{3} was observed.

Keywords: concentrated solar energy, thermochemical water splitting, hydrogen, density functional theory, perovskite
INTRODUCTION

Solar thermochemical hydrogen (STCH) production has been studied as a potential path to produce alternative fuels (Miller et al., 2014). This reaction is generally a two-step process that generates hydrogen (H₂) gas by splitting water using metal oxide materials and concentrated solar energy (Steinfeld, 2005; Smestad and Steinfeld, 2012). In the first step of a typical STCH cycle, the metal oxide is thermally reduced under inert atmosphere at high temperature (>1,200°C, achieved using concentrated solar-thermal flux), creating oxygen vacancies in the metal oxide and releasing oxygen gas (Scheffe and Steinfeld, 2014). In the second re-oxidation step at a lower temperature under steam, the oxygen-deficient metal oxide splits water to produce H₂ gas while regenerating the metal oxide for consecutive water splitting cycles. While a combined photovoltaic/electrolytic system can potentially exceed the efficiency of STCH systems were predicted to potentially exceed the efficiency of the combined system (Siegel et al., 2013).

Different classes of materials have been studied demonstrating STCH capabilities, including fluorites (CeO₂) (Gauckler et al., 1997; Abanades et al., 2010; Chueh et al., 2010; Scheffe and Steinfeld, 2014; Rao and Dey, 2017), iron oxides (Fe₃O₄) (Nakamura, 1977; Kodama et al., 2004; Coker et al., 2011; Scheffe and Steinfeld, 2014), and spinel ferrites (MFe₂O₄, M = Cu, Ni, Zn, etc.) (Tamura et al., 1995; Allendorf et al., 2008; Miller et al., 2008; Fresno et al., 2009; Scheffe and Steinfeld, 2014). Additionally, perovskite oxides (ABO₃) have been investigated heavily with many perovskite materials demonstrated to possess water splitting capabilities (McDaniel et al., 2013; Yang et al., 2014; Rao and Dey, 2017; Barcellos et al., 2018; Nair and Abanades, 2018; Qian et al., 2020a; Qian et al., 2020b). A large chemical space of perovskite materials is available due to the flexibility in chemical compositions and crystal structures the formula can stabilize (Vasala and Karpinnen, 2015). For this reason, perovskite oxides are fertile ground for discovering new STCH materials with high efficiencies.

With the vast composition space of inorganic materials, preliminary computational materials screening has become an important tool for accelerating materials discovery. Computational methods were previously applied to materials screening for the solid-state hydrogen storage reaction and chemical looping process (Clary et al., 2020; Singstock et al., 2020). For STCH, ternary (ABO₃) and quaternary (AA′BO₃) perovskites were explored to computationally evaluate their oxygen vacancy formation energies, electronic properties, and thermodynamic stabilities, with several promising candidate materials predicted based on these results (Emery et al., 2016; Sai Gautam et al., 2020). In this work, we report Gd₀.₅La₀.₅Co₀.₅Fe₂₅O₃ (GLCF) as a new STCH material that was discovered using a computational screening approach and experimentally demonstrated as a STCH producing material.

METHODS

Computational Screening Framework

Potential STCH compounds from the A₂BB′O₆, AA′B₂O₆ and AA′BB′O₆ compositional spaces were first screened for stability as perovskites using the machine learned descriptor τ (Bartel et al., 2019). τ classifies potential perovskite compositions as perovskite or non-perovskite using the Shannon radii (rA, rB, rX) of the A, B, and X site ions and the formal oxidation state of the A site cation as inputs. This descriptor exhibits 92% accuracy for predicting theoretical perovskite synthesizability for ABX₃ compositions and 91% accuracy for A₂BB′X₆ compositions, where fractional weighting of the B site cation radii is used (Bartel et al., 2019). Of the compounds identified by τ as synthesizable as perovskites, the STCH relevant properties of >1,000 Gd-containing compositions were evaluated in a high-throughput optimization scheme (Bare et al., 2021a). The compositions La₂CoFeO₆, GdLaCoFeO₆ and Gd₃CoFeO₆ are predicted by τ to be stable as perovskites (with formal oxidation states of +3 used for Gd, La, Co, and Fe and -2 used for O) and are predicted by DFT to have favorable STCH properties (see Results and Discussion).

PySPuDS (Bare et al., 2021b), a custom high-throughput python wrapper for the bond valence method (BVM) based Structure Prediction and Diagnostic Software (SPuDS), was used to generate initial perovskite geometries for DFT optimization (Lufaso and Woodward, 2001). The BVM Global Instability Index (GII), which SPuDS minimizes to predict the phase and magnitude of perovskite octahedral tilting, is strongly correlated with DFT energy in perovskite oxides (Morelock et al., 2021). This enables SPuDS to accurately predict perovskite ground state polymorph structures consistent with DFT, thereby substantially reducing the computational expense associated with high-throughput DFT investigations (Bare et al., 2021b). Initial geometries for DFT optimizations of the La₂CoFeO₆, GdLaCoFeO₆, and Gd₃CoFeO₆ perovskites were generated in the a-b-a Glazer mode, as this is the ground state tilting mode most frequently predicted by DFT for experimentally observed ABO₃ perovskite oxides (Bare et al., 2021b). Atomic configurations for cation alloying on the B site were generated using rock salt site ordering, while configurations for alloying on the A sites were generated that minimize the Ewald sum.

The specific pseudopotentials and Hubbard +U parameters used for GGA+U DFT optimizations are compatible with the Materials Project (MP) database (Jain et al., 2013), which tabulates the structures and energies of >130,000 inorganic materials. Calculations were performed using the Vienna Ab initio Simulation Program (VASP) 5.4.1 (Kresse and Hafner, 1993; Kresse and Hafner, 1994; Kresse and Furthmüller, 1996a; Kresse and Furthmüller, 1996b) with periodic boundary conditions utilizing projector augmented wave (PAW) pseudopotentials (Kresse and Joubert, 1999) and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional (Perdew et al., 1996). +U parameters of 3.32 and 5.3 were used for Co³⁺ and Fe³⁺, respectively, consistent with pymatgen’s MPRelaxSet (Jain et al., 2013). The electronic wave functions were expanded in a plane wave basis with an energy cutoff of 520 eV. The Brillouin
zones were sampled during geometry optimizations using an automatically generated Γ-centered Monkhorst-Pack k-point mesh with a grid density of at least 1,000/(atoms/unit cell). Oxide-specific corrections to DFT total energies were included to maintain compatibility with the MP (Jain et al., 2013).

We explicitly considered the effects of magnetism by first performing two consecutive spin-polarized relaxations initialized in a high-spin ferromagnetic configuration with species-specific initial magnetic moments dictated by the default MP spin parameters. Then, magnetic sampling of the computed initial magnetic moments dictated by the default MP spin (10°C/min), isothermally held for 30 min, then cooled to 200°C (25°C/min). For repeated consecutive analyses, the sample was re-performing two consecutive spin-polarized relaxations initialized with lattice vectors and initial magnetic moments fixed from previous optimizations–were optimized such that total energies were converged to within $10^{-6}$ eV, and forces converged to within 0.01 eV/Å. The effects of spin configuration on the electronic density of states (DOS) were also explicitly described in this manner. Calculations to determine oxygen vacancy energies were performed using the aforementioned convergence criteria for all symmetrically unique vacancies at a defect concentration of $C_d = 0.0833$.

**Materials**

All chemicals and gases were purchased and used as-received: gadolinium (III) oxide (Gd$_2$O$_3$, Alfa Aesar, 99.999%), lanthanum (III) oxide (La$_2$O$_3$, Aldrich, 99.99%), cobalt (II, III) oxide (Co$_3$O$_4$, Alfa Aesar, 99.99%), and iron (III) oxide (Fe$_2$O$_3$, Acros Organics, 99.99%), argon gas (Matheson, UHP grade), and air (Matheson, ultra-zero grade).

**Synthesis of Gd$_{0.5}$La$_{0.5}$Co$_{0.5}$Fe$_{0.5}$O$_3$**

Synthesis was conducted via a solid state synthesis route. For a 2 g scale reaction, stoichiometric amounts of gadolinium (III) oxide (0.7151 g), lanthanum (III) oxide (0.6427 g), cobalt (II, III) oxide (0.3167 g), and iron (III) oxide (0.3150 g) were ground by hand in an agate mortar and pestle for ~10 min. The resulting powder mixture was calcined in air at 600°C (5°C/min, 12 h dwell), then sintered in air at 1,300°C (9°C/min, 12 h dwell) with intermediate grinding.

**Characterization**

Powder X-ray diffraction (XRD) was collected on Bruker D2 Phaser X-ray Diffractometer with Cu Ka radiation. Profile fitting of diffraction patterns were performed with GSAS-II (Toby and Von Dreede, 2013). Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449 F1 Jupiter thermal analyzer.

Thermochemical cycling experiments were conducted under gas flow rates of 100 ml/min. For thermal reduction under Ar (100 ml/min), the sample (~50 mg) was first heated to 1,250°C (10°C/min), held isothermally for 30 min (thermal reduction), cooled to 400°C (25°C/min), then held isothermally for 30 min. For re-oxidation, the gas was switched to a mixture of air (80 ml/min) and Ar (20 ml/min), and the sample was heated to 1,100°C (10°C/min), isothermally held for 30 min, then cooled to 200°C (25°C/min). For repeated consecutive analyses, the sample was re-weighed between runs. TGA baseline correction was performed with an empty crucible. All thermograms shown here are corrected.

Water splitting experiments were conducted in a stagnation flow reactor (SFR) equipped with a laser-based sample heater and a mass spectrometer; the experimental details are described in previous papers (Scheffe et al., 2011; Arifin et al., 2012; Scheffe et al., 2013). In brief, the powder sample was placed in a tube furnace to maintain the oxidation temperature, and then irradiated by an IR laser through an optical access window to achieve the desired reduction temperature. The amount of oxygen gas evolved during reduction under Ar and hydrogen gas evolved during oxidation under 40 vol% steam were measured using a mass spectrometer.

High temperature XRD (HT-XRD) was performed on a Scintag PAD X-ray diffractometer, equipped with a Buehler hot-stage with Pt/Rh heating strip and surround heater. The hot stage resides within a sealed chamber with an X-ray-transparent beryllium window, and gas flow (either helium or air) was maintained at 200 ml/min. The data was analyzed using MDI Jade 8.2 software, and the plot was constructed with square root of intensity to easily observe low intensity peaks.

**RESULTS AND DISCUSSION**

To evaluate compound stability relative to decomposition, the DFT computed energies of the La$_2$CoFeO$_6$ (L2CF), GdLaCoFeO$_6$ (GLCF), and Gd$_2$CoFeO$_6$ (G2CF) perovskites optimized in the monoclinic, triclinic, and monoclinic space groups, respectively, (Supplementary Figure S1) were compared to the DFT computed energies of their potential decomposition products tabulated in the MP database. The energy of a material relative to the convex hull, $E_{\text{hull}}$, quantifies a material’s stability relative to its decomposition products. Monoclinic L2CF, triclinic GLCF, and monoclinic G2CF exhibit $E_{\text{hull}}$ of 0, 6.8, and 0 meV/atom, respectively, predicting that all three STCH candidates can be successfully synthesized as perovskites relative to their competing phases. The combination of the τ-predicted stabilities and $E_{\text{hull}}$ values of L2CF, GLCF, and G2CF suggests that Gd-La-Co-Fe-O is a promising compositional space for experimentally synthesizable perovskite oxides. We thus selected L2CF, GLCF, and G2CF from our high-throughput screening and computed additional STCH-relevant properties for these compounds, including DOS and charge neutral oxygen vacancy formation enthalpies ($\Delta H_{\text{OVac}}$).

The distributions of $\Delta H_{\text{OVac}}$ computed by DFT for the symmetrically unique sites of L2CF, GLCF, and G2CF are shown in Figure 1A. The $\Delta H_{\text{OVac}}$ distribution of GLCF is bounded by the $\Delta H_{\text{OVac}}$ distributions of L2CF (lower bound) and G2CF (upper bound). Herein, we use the DFT computed $\Delta H_{\text{OVac}}$ of CeO$_2$ (3.95 eV/atom) (Abanades and Flamant, 2006; Chueh and Haile, 2010), the gold standard STCH redox mediator (Muhich et al., 2016), as the upper bound for the STCH active range and a liberal lower bound of 2 eV/atom to account for uncertainty in DFT energetics (Naghavi et al., 2020). Materials approaching the minimum $\Delta H_{\text{OVac}}$ for STCH activity exhibit slow oxidation kinetics and/or degradation during redox cycling,
whereas materials approaching the maximum $\Delta H_{Ovac}$ for STCH activity suffer from reduced $H_2$ capacity (Muhich et al., 2016). GLCF exhibits both O vacancies with low and high $\Delta H_{Ovac}$, where vacancies with low $\Delta H_{Ovac}$ participate in $H_2$ production and those with high $\Delta H_{Ovac}$ are less likely to form under STCH operating conditions and therefore enable preservation of the perovskite lattice during redox cycling. This $\Delta H_{Ovac}$ distribution predicts enhanced cyclability of GLCF relative to L2CF and increased $H_2$ production capacity relative to G2CF.

Additionally, GLCF exhibits a large DOS effective mass, $m_e$, that arises from its large concentration of accessible electronic states near the conduction band minimum (CBM). Lany showed that large $m_e$ corresponds with large electronic contributions to the entropy of reduction $S_{red}$ in STCH processes (Lany, 2018) that fits STCH performance at high temperatures (Meredig and Wolverton, 2009). Figure 1B shows the DFT computed DOS for L2CF, GLCF, and G2CF. GLCF exhibits a larger multiplicity of Gd-f orbitals closer to the conduction band minimum than La-f orbitals is shown, leading to the largest calculated DOS electron effective mass at 1000 K ($m_e = 8.356$).

The room temperature XRD pattern of the synthesized GLCF is shown in Figure 2. The resulting material is isostructural to the orthorhombic perovskite, LaFeO$_3$ (Proskurnina et al., 2007; Wiglusz et al., 2015; Orlov et al., 2016). LeBail profile fitting analysis was performed, confirming the GLCF crystallizes in the Pbnm space group (No. 62) with no additional secondary phases. The lattice parameters for GLCF ($a = 5.3973(3)$ Å, $b = 5.4605(3)$ Å, $c = 7.6455(4)$ Å) are obtained. The $\delta$ in Gd$_0.5$La$_0.5$Co$_0.5$Fe$_0.5$O$_3$ relative to L2CF and increased $H_2$ production capacity relative to G2CF.

The room temperature XRD pattern of the synthesized GLCF is shown in Figure 2. The resulting material is isostructural to the LaFeO$_3$, Gd$_2$FeO$_4$, and La$_{0.8}$Gd$_{0.2}$FeO$_3$ (x = 0, 0.2, 0.5, 0.8, and 1), which are all orthorhombic perovskites (Proskurnina et al., 2007; Wiglusz et al., 2015; Orlov et al., 2016). LeBail profile fitting analysis was performed, confirming the GLCF crystallizes in the Pbnm space group (No. 62) with no additional secondary phases. The lattice parameters for GLCF ($a = 5.3973(3)$ Å, $b = 5.4605(3)$ Å, $c = 7.6455(4)$ Å) are obtained.
more gradual increase as the temperature was raised. The dip in the extent of reduction seen between 900 and 1,100°C is attributed to a phase change in the material, that is, formation of a phase at around 900°C that ejects oxygen to achieve stability. This change in δ is reproducible between cycles. The sample mass returns to the starting mass after the re-oxidation step.

The water splitting capability of GLCF was verified using a stagnation flow reactor (SFR). Figure 4 shows the water splitting results performed with a thermal reduction temperature (TR) of 1,350°C for 330 s and re-oxidation temperatures (TO) of 850 and 1,000°C for 1,200 s under 40 vol% H2O. Water splitting was observed under both sets of conditions, with the amount of H2 produced increasing with each cycle. For TO = 850°C (Figure 4A), the amount of H2 produced was 67, 90, and 101 μmol/g for each consecutive cycle. Moreover, significantly less O2 was released in the second reduction cycle compared to the first cycle, likely due to the water splitting step being kinetically limited. This is also evident from the long tails of H2 gas evolved during the re-oxidation steps. For TO = 1,000°C (Figure 4B), the H2 capacity increased (127 and 141 μmol/g), evident of an improvement in the rate of water splitting at higher temperature. Similar to the TO = 850°C experiment, more H2 was produced as cycle-number increased. In an ideal situation, once steady state has been achieved, the amount of H2 should be twice of the amount of O2 produced. From the SFR experiments with repeated cycles, GLCF is evolving and approaching this ideal steady state, though additional studies are needed to understand this behavior.

While LaFeO3 was previously reported to have negligible solar thermochemical H2O and CO2 conversion behavior (Jiang et al., 2014; Chen et al., 2017), similar perovskites to GLCF, La0.6Sr0.4Co0.2Fe0.8O3 and LaFe0.75Co0.25O3, were shown to be active for solar thermochemical CO2 conversion (STCH activity is unknown) (Nair and Abanades, 2018), indicating that the mixing of Co and Fe may have contributed to the solar thermochemical conversion activity. For La0.6Sr0.4Co0.2Fe0.8O3 and LaFe0.75Co0.25O3, however, CO production decreased substantially during subsequent cycles (Nair and Abanades, 2018). The substitution of Gd for La may have contributed to minimizing performance degradation as predicted by DFT calculations.

In terms of its water splitting ability, at TR = 1,350°C and TO = 850°C, GLCF produced more H2 (101 μmol/g) than CeO2 (50 μmol/g) (Barcellos et al., 2018). However, GLCF produced less H2 compared to the previously studied perovskite materials BaCe0.25Mn0.75O3 (BCM) and Sr0.6La0.4Mn0.6Al0.4O3 (SLMA4664) (McDaniel et al., 2013; Barcellos et al., 2018). BCM and SLMA4664 produced 140 μmol/g (TR = 1,350°C, TO = 850°C) and 307 μmol/g (TR = 1,350°C, TO = 1,000°C) of H2, respectively (McDaniel et al., 2013; Barcellos et al., 2018). However, direct comparisons of performance reported for different conditions (temperature, atmosphere, and time) for various materials that have different optimized conditions for STCH can lead to incorrect conclusions about the H2 production capabilities of candidate materials. In the present case, the water splitting experimental conditions implemented for GLCF have not yet been optimized. Nevertheless, computational screening

![Figure 4](image-url)
greatly accelerated the discovery of GLCF as a water splitting material, which would otherwise have been experimentally time consuming due to the vast chemical space of perovskite materials.

To understand the phase stability in GLCF during redox cycling, HT-XRD patterns were collected first from room temperature to 1,250°C to 50°C under He for thermal reduction, then with an identical temperature profile under air for re-oxidation. The GLCF sample was redox-cycled (T_R = 1,250°C under Ar, T_O = 1,100°C under air) before collecting the HT-XRD patterns. The HT-XRD patterns are shown in Figure 5. During the HT-XRD experiment, GLCF appears to maintain its perovskite phase as the major phase, but the major peaks broaden and exhibit some peak splitting occurring during reduction. In addition to the changes in the major GLCF phase, during cool down at ∼1,200°C under He, additional peaks appear corresponding to Gd_2O_3 phase. Due to the shift in peaks, it may have different chemistry (i.e. Gd_{2-x}La_xO_3). The additional Gd_2O_3 phase remains in the pattern until heated under air at ∼700–800°C during re-oxidation. The disappearance of the Gd_2O_3 phase may correspond to the increase in the extent of reduction observed in the TG experiment at ∼900°C during reoxidation. Moreover, a spinel phase appears during cool down under air. Overall, during the redox cycle, the perovskite phase persists, agreeing with the stable STCH activity observed in the SFR results and TGA cycling tests.

**CONCLUSION**

Solar thermochemical hydrogen production (STCH) significantly contributes to the renewable energy portfolio. However, materials discovery with high efficiency is needed, and computational screening can greatly accelerate this process. This was demonstrated with Gd_{0.5}La_{0.5}Co_{0.5}Fe_{0.5}O_3 (GLCF), a perovskite oxide, that was computationally determined first, then experimentally demonstrated. When compared to LaCo_{0.5}Fe_{0.5}O_3, it was predicted that GLCF would have higher phase stability due to the incorporation of Gd on the La site. The synthesis of a single phase GLCF sample was achieved. With redox activity confirmed through thermogravimetric analysis, stable water splitting behavior over multiple cycles was also observed. When compared to LaCo_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3 and LaFe_{0.75}Co_{0.25}O_3, which suffered from performance degradation with subsequent cycles, the Gd substitution of La plays a significant role to maintain water splitting performance. Based on high temperature x-ray diffraction experiments, the GLCF perovskite phase persists which potentially contributes to the stable water splitting performance. This work demonstrates that computational materials screening can greatly accelerate the discovery of new water splitting materials. Through computational screening, potential water splitting materials were narrowed down to a promising STCH material from the vast chemical space of perovskite materials, and a unique strategy of incorporating a rare earth element that improved the stability was demonstrated.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.
AUTHOR CONTRIBUTIONS

JP conducted material synthesis and characterization and drafted the manuscript. ZB and RM conducted the DFT calculations and wrote sections of the manuscript. MR, AM, and EC conducted materials characterization. AA provided guidance on material synthesis. CM supervised the DFT calculations.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenrg.2021.750600/full#supplementary-material

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