Co-precipitation synthesized nanostructured Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials for solar thermochemical conversion of CO$_2$ into fuels

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ABSTRACT

Synthesis, characterization, and application of Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials (where, Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Er) for the thermochemical conversion of CO$_2$ reported in this paper. The Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials were synthesized by using an ammonium hydroxide-driven co-precipitation method. The derived Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials were characterized via powder X-ray diffraction, scanning electron microscope, and electron diffraction spectroscopy. The characterization results indicate the formation of spherically shaped Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ nanostructured particles. As-prepared Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials were further tested toward multiple CO$_2$ splitting cycles by utilizing a thermogravimetric analyzer. The results obtained indicate that all the Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials produced higher quantities of O$_2$ and CO than the previously studied pure CeO$_2$ and lanthanide-doped ceria materials. Overall, the Ce$_{0.911}$La$_{0.053}$Ag$_{0.047}$O$_{1.925}$ showed the maximum redox reactivity in terms of O$_2$ release (72.2 $\mu$mol/g cycle) and CO production (136.6 $\mu$mol/g cycle).

List of symbols

| Symbol | Description |
|--------|-------------|
| $n_{O_2}$ | Moles of O$_2$ ($\mu$mol/g) |
| $n_{CO}$ | Moles of CO ($\mu$mol/g) |
| $\Delta m_{\text{loss}}$ | Amount of loss in the mass (mg) |
| $\Delta m_{\text{gain}}$ | Amount of gain in the mass (mg) |
| $M_{O_2}$ | Molecular weight of O$_2$ (g/mol) |
| $M_0$ | Molecular weight of O (g/mol) |
| $m_{\text{Ce}_{0.9}\text{Ln}_{0.05}\text{Ag}_{0.05}\text{O}_{2-\delta}}$ | Mass of the Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials (mg) |

Introduction

The worldwide human population is rising at a quick pace, which inherently demands a large amount of energy for consumption [1]. Current energy production largely depends on the utilization of fossil fuels. The excessive use of petroleum-based resources results in a continuous CO$_2$ discharge [2, 3]. This constant release of CO$_2$ is considered as one of the...
primary reasons for the variation in the climate parameters [4]. The environmental distress occurring due to increases in CO₂ emission generated more interest in the conversion of CO₂ into value-added products.

One of the possible options for CO₂ utilization is to convert the captured CO₂ into fuels. Solar thermochemical cycles driven based on the metal oxide (MO)-based redox reactions can split CO₂ into CO (Fig. 1) [5, 6]. The solar CO produced can be combined with the solar H₂ (produced via solar thermochemical splitting of water) for the manufacturing of the solar syngas, which can be further utilized in the catalytic Fischer–Tropsch process [7].

The MO-based solar-driven thermochemical conversion of CO₂ is a two-phase process. In the first phase, the MO is reduced with the help of concentrated solar power, and in phase 2, the reduced MO is re-oxidized again via a CO₂ splitting reaction. Zinc oxide [8, 9], tin oxide [10, 11], iron oxide [12, 13], CeO₂ [14–16], doped ceria [17–20], perovskites [25–28], and others [29–32] have been utilized for the solar thermochemical conversion of H₂O and CO₂. Among all these, the phase pure CeO₂ is considered as one of the promising options due to its faster reaction kinetics and better thermal stability. Although the CeO₂ is beneficial for the thermochemical conversion of H₂O and CO₂, a lower fuel production capacity is one of the major limitations associated with this MO.

Recently, Bhosale and Takalkar [33] reported that the doping of lanthanides such as La, Pr, Nd, Sm, Gd, Tb, Dy, and Er into CeO₂ fluorite cubic crystal structure improved the thermal reduction (TR) capacity of the CeO₂. It was also reported that although the TR capability of CeO₂ was improved, only Ce₀.₉La₀.₁O₂ was capable of producing higher quantities of CO than CeO₂ via CO₂ splitting reaction. In another investigation, Takalkar et al. [19] reported that the inclusion of Ag in the transition metal-doped ceria considerably improved the TR as well as CO₂ splitting (CDS) capacity.

Based on the results reported in our previous investigations, in this study, the synthesis, characterization, and application of Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂–δ materials (where, Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Er) for the thermochemical conversion of CO₂ is reported. Synthesis of the Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂–δ materials is achieved via a co-precipitation method. The derived materials are further tested for multiple thermochemical CDS cycles by utilizing a thermogravimetric analyzer (TGA) setup. The TR and CDS capacity of the Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂–δ materials was estimated and compared with the previously studied phase pure CeO₂ and lanthanide-doped ceria materials.

**Experimental**

**Preparation and characterization of Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂–δ**

Nitrate-based precursors of ceria, silver, and all lanthanides were acquired from Sigma-Aldrich, USA.

![Figure 1](image-url) Overall process of production of liquid fuels by using solar syngas generated via MO-based solar thermochemical H₂O/CO₂ splitting cycle.
Aqueous 28% NH$_3$OH as a precipitating agent was procured from the same supplier. Ultrapure deionized (DI) water (produced through Direct-Q system, Millipore, France) was utilized for the preparation of nitrate solution. An ultrapure grade Ar gas (purity 99.999%) and 50% CO$_2$ + 50% Ar gas mixture are ordered from the Buzwair Scientific and Technical Gases, Doha, Qatar.

The synthesis of redox Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials was achieved via co-precipitation of the hydroxide method. As shown in Fig. 2, an aqueous mixture of selected metal precursors was prepared by dissolving them in 300 ml of deionized water. To this mixture, aqueous ammonium hydroxide (28%) was added to attain a pH approximately equal to 10. The mixture further stirred for 24 h with a maintained pH ~ 10. Once the stirring was stopped, the precipitate of Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ material was allowed to settle via gravity (mixture kept undisturbed overnight). The next morning, the supernatant liquid was decanted, and the obtained precipitate was washed several times by deionized water with the help of a vacuum filtration unit. The obtained filtered cake of Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ was dried (120 °C, 5 h), crushed, and annealed (Nabertherm Furnace) up to 1000 °C for 4 h in the presence of air. The obtained annealed powder was analyzed for the determination of the phase/elemental composition and morphology by using Panalytical X'Pert powder X-ray diffractometer (PXRD) and scanning electron microscope (SEM, Nova Nano 450, FEI) equipped with the electron diffraction spectroscopy (EDS).

**CO$_2$ splitting experiments**

The Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials were experimentally tested in a TGA setup (Setaram Instrumentation, France), which is shown in Fig. 3. The experimental parameters utilized to perform the thermochemical cycles are given in Table 1. Approximately, 50 mg of the calcined Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ powder was charged in an alumina (100 μl) crucible, and then placed inside the heating furnace of the TGA. Before performing the TGA experiments, the residual air filling the hollow space near to the furnace was evacuated by applying a vacuum followed by sweeping by the inert Ar. Chilled water (generated by Julabo FC 1600T) was utilized to decrease the exiting gas stream temperature. Additional details related to the TGA setup and the experimental procedure are already described in our previous studies [23, 29]. Multiple TR and CDS steps were performed by considering the operating parameters given in Table 1.

The mass variations allied with the Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials during the TR and CDS steps were documented after subtracting the blank TGA experimental data from the actual TGA experimental

Figure 2 Synthesis of Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials via the co-precipitation method.

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The amount of O₂ liberated (μmol/g) during the TR step and the quantity of CO produced during the CDS step are calculated by utilizing Eqs. (1) and (2).

\[
\begin{align*}
  n_{O_2} &= \frac{\Delta m_{\text{loss}}}{(M_{O_2} \times m_{\text{Ce}_{0.9}\text{Ln}_{0.05}\text{Ag}_{0.05}\text{O}_{2-\delta}})} \quad (1) \\
  n_{CO} &= \frac{\Delta m_{\text{gain}}}{(M_{O} \times m_{\text{Ce}_{0.9}\text{Ln}_{0.05}\text{Ag}_{0.05}\text{O}_{2-\delta}})} \quad (2)
\end{align*}
\]

**Results and discussion**

After synthesizing the Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂₋δ materials, the next important step was to determine the phase composition of the derived materials. PXRD profiles of the calcined Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂₋δ materials are shown in Fig. 4a, b. The presented patterns indicate a cubic fluorite crystal structure of the Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂₋δ materials, similar to the one reported in the case of CeO₂ [23]. The PXRD profiles shown in Fig. 4a further indicates the absence of the formation of any metal or metal oxide impurities. As shown in Fig. 4b, the Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂₋δ material peaks shift toward either lower or higher 2θ angle (based on the crystal ionic radii of the dopants). This shift in the peaks further confirmed the successful incorporation of the dopants inside the ceria fluorite crystal structure. The formation of nominally phase pure Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂₋δ materials was also assured via EDS analysis (results given in Table 2).

In order to determine the crystallite size, a widely used Scherrer equation and the PXRD data associated with the Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂₋δ materials were utilized.
Table 2 indicates that the variation in the crystallite size of the Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_2\)–\(\delta\) materials does not follow any specific trend. As per the obtained results, the Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_2\)–\(\delta\) materials can be arranged as follows based on their average crystallite size: La\(_{5}\)Ag\(_{5}\)Ce > Dy\(_{5}\)Ag\(_{5}\)Ce > Sm\(_{5}\)Ag\(_{5}\)Ce > Pr\(_{5}\)Ag\(_{5}\)Ce > Tb\(_{5}\)Ag\(_{5}\)Ce > Gd\(_{5}\)Ag\(_{5}\)Ce > Er\(_{5}\)Ag\(_{5}\)Ce > Nd\(_{5}\)Ag\(_{5}\)Ce.

After estimating the composition and crystallite size of each Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_2\)–\(\delta\) material, the morphology was scrutinized by performing the SEM analysis. The SEM images obtained looks very similar to each other and indicate the formation of roughly spherical particles of Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_2\)–\(\delta\). The microscopic SEM analysis further confirmed that the particles were agglomerated. It was also observed that the average particle size was very close to the crystallite sizes given in Table 2. The representative SEM images of Pr\(_{5}\)Ag\(_{5}\)Ce, Tb\(_{5}\)Ag\(_{5}\)Ce, Gd\(_{5}\)Ag\(_{5}\)Ce, and Er\(_{5}\)Ag\(_{5}\)Ce are shown in Fig. 5.

The redox performance of the Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_2\)–\(\delta\) materials is estimated by performing the thermochemical CDS experiments using the TGA setup. Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_2\)–\(\delta\) materials thermally reduced at 1400 \(^\circ\)C (10 K/min) for 60 min in the presence of the inert Ar (100 ml/min) and then re-oxidized at 1000 \(^\circ\)C by using a feed gas mixture containing 50% CO\(_2\) + 50% Ar (100 ml/min). As an example, Fig. 6 represents a TGA profile of La\(_{5}\)Ag\(_{5}\)Ce material obtained during the first CDS cycle. As shown in Fig. 6, during the TR step, the mass of the La\(_{5}\)Ag\(_{5}\)Ce material reduced by 0.511 mg, and during the CDS step, the weight of the La\(_{5}\)Ag\(_{5}\)Ce material increased by 0.126 mg. These mass variations further converted into respective redox performances in terms of \(n_{O_2}\) released (320.2 \(\mu\)mol/g) and \(n_{CO}\) produced (157.8 \(\mu\)mol/g) by using Eqs. (1) and (2).

The mass variations associated with the Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_2\)–\(\delta\) materials recorded during the first cycle are shown in Fig. 7a, b. The \(n_{O_2}\) released and \(n_{CO}\) produced by each Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_2\)–\(\delta\) material was computed based on the obtained TGA profiles and given in Table 3. The data given in Table 3 show that the Pr\(_{5}\)Ag\(_{5}\)Ce was capable of releasing a higher amount of O\(_2\) at 1400 \(^\circ\)C than the other Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_2\)–\(\delta\) materials. Likewise, the CO production aptitude of La\(_{5}\)Ag\(_{5}\)Ce was the uppermost when compared with the remaining Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_2\)–\(\delta\) materials. The numbers listed in the \(n_{CO}/n_{O_2}\) ratio column shows that the re-oxidation ability of the
Nd₅Ag₅Ce was better than the other Ce₀.⁹Ln₀.⁰₅Ag₀.⁰₅O₂₋θ materials.

Interesting to note that the nCO produced by each Ce₀.⁹Ln₀.⁰₅Ag₀.⁰₅O₂₋θ material was considerably lower than the nO₂ released during the first cycle. The two probable reasons for these results are (a) poor re-oxidation ability of the Ce₀.⁹Ln₀.⁰₅Ag₀.⁰₅O₂₋θ materials or (b) additional mass loss during the first TR reduction due to the release of volatile chemicals from the Ce₀.⁹Ln₀.⁰₅Ag₀.⁰₅O₂₋θ materials (which remained unburnt during the calcination step). For further investigation of this matter, the Ce₀.⁹Ln₀.⁰₅Ag₀.⁰₅O₂₋θ materials were tested for three cycles (by maintaining the same operating conditions utilized in

**Table 2** Abbreviations, chemical composition, crystallite size, and cell parameter of each Ce₀.⁹Ln₀.⁰₅Ag₀.⁰₅O₂₋θ material

| Abbreviations | Ce₀.⁹Ln₀.⁰₅Ag₀.⁰₅O₂₋θ composition (via EDS) | Crystallite size (nm) | Cell parameter (Å) |
|---------------|---------------------------------------------|----------------------|-------------------|
| La₅Ag₅Ce      | Ce₀.⁹₁₁La₀.⁰₅₃Ag₀.⁰₄₇O₁.⁹₂₅                  | 63.1                 | 5.4₃₄             |
| Pr₅Ag₅Ce      | Ce₀.⁸₈₂Pr₀.⁰₅₁Ag₀.⁰₅₁O₁.₈₈₆                  | 46.₆                 | 5.₄₁₁             |
| Nd₅Ag₅Ce      | Ce₀.⁹₂₁Nd₀.⁰₄₉Ag₀.⁰₅₀O₁.₉₄₀                  | 3₂.₃                 | 5.₄₁₇             |
| Sm₅Ag₅Ce      | Ce₀.⁸₉₆Sm₀.⁰₄₈Ag₀.⁰₅₃O₁.₈₉₀                  | 6₀.₂                 | 5.₄₂₁             |
| Gd₅Ag₅Ce      | Ce₀.⁸₈₉Gd₀.⁰₄₄Ag₀.⁰₅₀O₁.₈₈₄                  | 3₉.₄                 | 5.₃₈₉             |
| Tb₅Ag₅Ce      | Ce₀.₉₀₅Tb₀.⁰₅₁Ag₀.⁰₄₆O₁.₉₀₉                  | 4₁.₃                 | 5.₄₁₀             |
| Dy₅Ag₅Ce      | Ce₀.₉₁₀Dy₀.⁰₅₃Ag₀.⁰₄₈O₁.₉₂₃                  | 6₁.₅                 | 5.₄₁₁             |
| Er₅Ag₅Ce      | Ce₀.₈₉₉Er₀.⁰₅₀Ag₀.⁰₅₅O₁.₀₀₀                  | 3₈.₁                 | 5.₄₁₁             |

**Figure 5** SEM images of Pr₅Ag₅Ce, Tb₅Ag₅Ce, Gd₅Ag₅Ce, and Er₅Ag₅Ce.
the case of the first cycle). Figure 8 shows the variations in the mass of the Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials during the successive three thermochemical cycles. Besides, Fig. 9a and b compares the $n_{O_2}$ released and $n_{CO}$ produced by each Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ material from cycle 1 to cycle 3.

Figures 8 and 9 show that the $n_{O_2}$ released by all the Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials during cycle 1 was considerably higher than cycle 2. For example, the $n_{O_2}$ released by La$_5$Ag$_5$Ce, Nd$_5$Ag$_5$Ce, Gd$_5$Ag$_5$Ce, and Dy$_5$Ag$_5$Ce in cycle 2 was lower by 77.9%, 64.6%, 76.6%, and 80.0% as compared to cycle 1. The comparison between cycle 2 and cycle 3 shows a different story. The $n_{O_2}$ released by all the Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials in cycle 3 was slightly less when compared to cycle 2. For instance, the $n_{O_2}$ released by La$_5$Ag$_5$Ce, Nd$_5$Ag$_5$Ce, Gd$_5$Ag$_5$Ce, and Dy$_5$Ag$_5$Ce in cycle 3 was lower by 2.0%, 0.0%, 14.8%, and 1.8% than cycle 2. Based on the results given in Figs. 8 and 9, it can be concluded that the prime reason for the more substantial $O_2$ evolution in cycle 1 was the additional loss in the mass of the Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials due to the release of volatile chemicals.

In the case of the CDS step, the $n_{CO}$ produced by each Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ material first decreased in cycle 2 (compared to cycle 1) and remained approximately stable in cycle 3 (compared to cycle 2). For example, the $n_{CO}$ produced by La$_5$Ag$_5$Ce, Nd$_5$Ag$_5$Ce, Gd$_5$Ag$_5$Ce, and Dy$_5$Ag$_5$Ce in cycle 2 was 11.1%, 20.0%, 7.4%, and 24.5% lower than cycle 1. In contrast, the %decrease in the $n_{CO}$ produced by La$_5$Ag$_5$Ce, Nd$_5$Ag$_5$Ce, Gd$_5$Ag$_5$Ce, and Dy$_5$Ag$_5$Ce in cycle 3 was dropped to 1.1%, 0.5%, 0.9%, and 1.2% when compared with the cycle 2 data. The $n_{CO}/n_{O_2}$ ratio of all the Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials increased significantly in cycle 2 when compared with cycle 1. For instance, the $n_{CO}/n_{O_2}$ ratio of La$_5$Ag$_5$Ce, Nd$_5$Ag$_5$Ce,
Gd5Ag5Ce, and Dy5Ag5Ce increased by 1.49, 1.01, 1.13, and 1.09 in cycle 2 when compared with cycle 1. The $n_{\text{CO}}/n_{\text{O}_2}$ ratio of all the Ce0.9Ln0.05Ag0.05O2–δ materials in cycle 2 and cycle 3 were almost identical.

The results obtained during cycle 3 indicate that most of the Ce0.9Ln0.05Ag0.05O2–δ materials are moving toward achieving a stable redox reactivity. For attaining further confirmation about the stable redox reactivity, the Ce0.9Ln0.05Ag0.05O2–δ materials were tested for ten successive cycles. The TGA profiles associated with the ten cycles are shown in Fig. 10. It was already confirmed that the data obtained in cycle 1 is misleading, and hence the TGA analysis was more focused on the remaining nine cycles. The $n_{\text{O}_2}$

Table 3 Redox performance of Ce0.9Ln0.05Ag0.05O2–δ materials during the first cycle

| Ce0.9Ln0.05Ag0.05O2–δ | $n_{\text{O}_2}$ released (μmol/g) | $n_{\text{CO}}$ produced (μmol/g) | $n_{\text{CO}}/n_{\text{O}_2}$ ratio |
|------------------------|-----------------------------------|-----------------------------------|-------------------------------------|
| La5Ag5Ce               | 320.0                             | 157.8                             | 0.49                                |
| Pr5Ag5Ce               | 548.6                             | 152.7                             | 0.28                                |
| Nd5Ag5Ce               | 191.0                             | 153.5                             | 0.80                                |
| Sm5Ag5Ce               | 195.3                             | 125.9                             | 0.64                                |
| Gd5Ag5Ce               | 326.5                             | 125.0                             | 0.38                                |
| Tb5Ag5Ce               | 212.3                             | 139.7                             | 0.66                                |
| Dy5Ag5Ce               | 365.8                             | 143.9                             | 0.39                                |
| Er5Ag5Ce               | 415.4                             | 134.1                             | 0.32                                |
released and \( n_{\text{CO}} \) produced by each Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_{2-\delta}\) material from cycle 2 to cycle 10 are shown in Figs. 11 and 12.

As per the data given in Fig. 11, the La\(_5\)Ag\(_5\)Ce, Pr\(_5\)Ag\(_5\)Ce, and Nd\(_5\)Ag\(_5\)Ce shows a stable release of O\(_2\) from cycle 2 to cycle 10. The Gd\(_5\)Ag\(_5\)Ce indicates redox stability in terms of constant O\(_2\) release from cycle 3 to cycle 10. For the rest of the Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_{2-\delta}\) materials, i.e., Sm\(_5\)Ag\(_5\)Ce, Tb\(_5\)Ag\(_5\)Ce, Dy\(_5\)Ag\(_5\)Ce, and Er\(_5\)Ag\(_5\)Ce, a steady \( n_{\text{O}_2} \) evolution was realized after cycle 5 or cycle 6. In terms of average \( n_{\text{O}_2} \) released from cycle 2 to cycle 10, La\(_5\)Ag\(_5\)Ce (72.2 \( \mu \text{mol} \) of O\(_2\)/g cycle) and Tb\(_5\)Ag\(_5\)Ce (60.2 \( \mu \text{mol} \) of O\(_2\)/g cycle) were observed to be the best and worst among all the Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_{2-\delta}\) materials.

As shown in Fig. 12, the La\(_5\)Ag\(_5\)Ce, Pr\(_5\)Ag\(_5\)Ce, Nd\(_5\)Ag\(_5\)Ce, Gd\(_5\)Ag\(_5\)Ce, and Dy\(_5\)Ag\(_5\)Ce showed a stable production of CO from cycle 2 to cycle 10. In contrast, a constant \( n_{\text{CO}} \) production in the case of Sm\(_5\)Ag\(_5\)Ce, Tb\(_5\)Ag\(_5\)Ce, and Er\(_5\)Ag\(_5\)Ce was noticed from cycle 6 to cycle 10. In terms of average \( n_{\text{CO}} \) produced from cycle 2 to cycle 10, the Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_{2-\delta}\) materials can be arranged as: La\(_5\)Ag\(_5\)Ce > Nd\(_5\)Ag\(_5\)Ce > Pr\(_5\)Ag\(_5\)Ce > Gd\(_5\)Ag\(_5\)Ce > Tb\(_5\)Ag\(_5\)Ce > Sm\(_5\)Ag\(_5\)Ce > Er\(_5\)Ag\(_5\)Ce > Dy\(_5\)Ag\(_5\)Ce.

According to the data given in Fig. 13, the re-oxidation ability (average \( n_{\text{CO}} / n_{\text{O}_2} \) ratio) of the La\(_5\)Ag\(_5\)Ce and Tb\(_5\)Ag\(_5\)Ce was the highest compared to the rest of the Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_{2-\delta}\) materials. Based on \( n_{\text{O}_2} \) released and \( n_{\text{CO}} \) produced from cycle 2 to cycle 10, the La\(_5\)Ag\(_5\)Ce appears to be the most excellent candidate among all the Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_{2-\delta}\) materials investigated in this study.

Table 4 reports the comparison of Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_{2-\delta}\) materials with the CeO\(_2\) and Ce\(_{0.9}\)Ln\(_{0.1}\)O\(_2\) materials. The results given in Table 4 shows that all the Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_{2-\delta}\) materials were capable of higher \( n_{\text{O}_2} \) release (except for Sm\(_5\)Ag\(_5\)Ce) and \( n_{\text{CO}} \) production than CeO\(_2\) and their corresponding Ce\(_{0.9}\)Ln\(_{0.1}\)O\(_2\) materials. For instance, the \( n_{\text{O}_2} \) released by La\(_5\)Ag\(_5\)Ce, Pr\(_5\)Ag\(_5\)Ce, Nd\(_5\)Ag\(_5\)Ce, Gd\(_5\)Ag\(_5\)Ce, Tb\(_5\)Ag\(_5\)Ce, Dy\(_5\)Ag\(_5\)Ce, and Er\(_5\)Ag\(_5\)Ce was higher by 21.8 \( \mu \text{mol} \) of O\(_2\)/g cycle, 23.1 \( \mu \text{mol} \) of O\(_2\)/g cycle, 23.0 \( \mu \text{mol} \) of O\(_2\)/g cycle, 18.6 \( \mu \text{mol} \) of O\(_2\)/g cycle, 0.20 \( \mu \text{mol} \) of O\(_2\)/g cycle, 12.1 \( \mu \text{mol} \) of O\(_2\)/g cycle, and 8.50 \( \mu \text{mol} \) of O\(_2\)/g cycle as compared to Ce\(_{0.9}\)La\(_{0.1}\)O\(_2\), Ce\(_{0.9}\)Pr\(_{0.1}\)O\(_2\), Ce\(_{0.9}\)Nd\(_{0.1}\)O\(_2\), Ce\(_{0.9}\)Gd\(_{0.1}\)O\(_2\), Ce\(_{0.9}\)Tb\(_{0.1}\)O\(_2\), Ce\(_{0.9}\)Dy\(_{0.1}\)O\(_2\), and Ce\(_{0.9}\)Er\(_{0.1}\)O\(_2\), respectively. Similarly, the La\(_5\)Ag\(_5\)Ce, Pr\(_5\)Ag\(_5\)Ce, Nd\(_5\)Ag\(_5\)Ce, Sm\(_5\)Ag\(_5\)Ce, Gd\(_5\)Ag\(_5\)Ce, Tb\(_5\)Ag\(_5\)Ce, Dy\(_5\)Ag\(_5\)Ce, and Er\(_5\)Ag\(_5\)Ce.

Figure 8 TGA profiles obtained for Ce\(_{0.9}\)Ln\(_{0.05}\)Ag\(_{0.05}\)O\(_{2-\delta}\) materials during three cycles.
Er$_5$Ag$_5$Ce produced 1.39, 1.44, 1.52, 1.32, 1.49, 1.43, 1.29, and 1.37 times higher CO when compared with the Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials, respectively. The overall results of this investigation indicate that the incorporation of Ag in the Ln-doped ceria was beneficial to improve the redox performance of Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials.

Summary and conclusions

The PXRD and EDS analysis have confirmed the formation of nominally phase pure Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials via co-precipitation of the hydroxide method. The average crystallite size of the derived Ce$_{0.9}$Ln$_{0.05}$Ag$_{0.05}$O$_{2-\delta}$ materials was in the range of 32–64 nm. The SEM analysis further established a
spherical nanostructured particle morphology of the Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂₋δ materials. The SEM analysis also indicates that the doping of the lanthanides and silver does not have any significant effect on the morphology of Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂₋δ materials. Based on the results associated with the TGA analysis, the redox reactivity of the Ce₀.₉Ln₀.₀₅Ag₀.₀₅O₂₋δ materials can be ranked as: Ce₀.₉₁₁La₀.₀₅₃Ag₀.₀₄₇O₁.₹₂₅ > Ce₀.₉₂₁Nd₀.₀₄₉Ag₀.₀₅₀O₁.₹₄₀ ~ Ce₀.₈₉₂Pr₀.₀₅₁Ag₀.₀₅₁O₁.₸₈₆ > Ce₀.₈₈₉Gd₀.₀₅₄Ag₀.₀₅₀O₁.₸₈₄ > Ce₀.₉₀₅Tb₀.₀₅₁O₁.₹₅₅.
Ag_{0.046}O_{1.909} > Ce_{0.896}Sm_{0.048}Ag_{0.053}O_{1.890} \sim Ce_{0.899}Er_{0.050}Ag_{0.055}O_{1.900} > Ce_{0.910}Dy_{0.053}Ag_{0.048}O_{1.923}. The TGA results also indicate that the Ce_{0.911}La_{0.053}Ag_{0.047}O_{1.925} and Ce_{0.905}Tb_{0.051}Ag_{0.046}O_{1.909} possess the highest re-oxidation ability as compared to the rest of the Ce_{0.9}Ln_{0.05}Ag_{0.05}O_{2−δ} materials. The overall results of this investigation indicate that the inclusion of Ag into the Ln-doped ceria considerably improved the O_2 releasing and CO production capability of the Ce_{0.9}Ln_{0.05}Ag_{0.05}O_{2−δ} materials as compared to the phase pure CeO_2 and Ce_{0.9}Ln_{0.1}O_2 materials. After estimating the CO production capacity, our research team is currently focused on the production of H_2 by using the Ce_{0.9}Ln_{0.05}Ag_{0.05}O_{2−δ} materials.
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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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