The redox reactivity of the Li-, Mg-, Na-, Ba-, Sr-, and Sn-doped ceria (Ce_{0.9}A_{0.1}O_{2-d}) toward thermochemical CO_2 splitting is investigated. Proposed Ce_{0.9}A_{0.1}O_{2-d} materials are prepared via co-precipitation of the hydroxide technique. The composition, morphology, and the average particle size of the Ce_{0.9}A_{0.1}O_{2-d} materials are determined by using suitable characterization methods. By utilizing a thermogravimetric analyzer setup, the long-term redox performance of each Ce_{0.9}A_{0.1}O_{2-d} material is estimated. The results obtained indicate that all the Ce_{0.9}A_{0.1}O_{2-d} materials are able to produce steady amounts of O_2 and CO from cycle 4 to cycle 10. Based on the average n_{O_2} released and n_{CO} produced, the Ce_{0.899}Sn_{0.1}O_{2.002} and Ce_{0.895}Ca_{0.099}O_{1.889} are observed to be the top and bottom-most choices. When compared with the CeO_2 material, all Ce_{0.9}A_{0.1}O_{2-d} materials showed elevated levels of O_2 release and CO production.
operating temperatures compared to direct thermolysis and utilization of the same MO in multiple cycles are some of the major advantages associated with the STCs. Besides, the H2/CO and O2 are produced in two different steps; hence, the need for a cost-intensive separation method is avoided. Previously, zinc oxide [10, 11], tin oxide [12, 13], iron oxide [14, 15], ceria and doped ceria [16, 17], ferrites [18–22], perovskites [23–27], and others [28–31] have been considered for the STCs. Among these MOs, ceria-based oxides showed long-term stability and faster reaction kinetics for multiple STCs. In general, the ceria-based oxides are some of the major advantages associated with the STCs. Besides, the H2/CO and O2 are produced in two different steps; hence, the need for a cost-intensive separation method is avoided. Previously, zinc oxide [10, 11], tin oxide [12, 13], iron oxide [14, 15], ceria and doped ceria [16, 17], ferrites [18–22], perovskites [23–27], and others [28–31] have been considered for the STCs. Among these MOs, ceria-based oxides showed long-term stability and faster reaction kinetics for multiple STCs. In general, the ceria-based oxide is thermally reduced by releasing lattice O2 at higher temperatures. This reduced ceria-based oxide is then re-oxidized either by WS or CS reaction resulting in the formation of H2 or CO.

Ceria was first investigated for the solar thermochemical conversion of H2O into H2 by Abanades and Flamant in 2006 [32]. Rhodes et al. [33] examined ceria toward the CS reaction in more than 2000 STCs. Chueh et al. [34] analyzed the redox reactivity (RR) of ceria in 500 cycles by using a cavity-receiver reactor driven by concentrated solar power. Venstrom et al. [35] studied the isothermal operation of ceria-based thermochemical CS by performing 100 cycles. Scheife and Steinfeld [36] thermodynamically scrutinized the application of Gd-, Y-, Sm-, Ca-, and Sr-doped ceria toward the splitting of H2O and CO2 at different temperatures and oxygen partial pressures. The H2 production capacity of the combustion synthesized Cu-, Ni-, Mn-, and Fe-doped ceria via thermochemical WS reaction was estimated by Kaneko et al. [37]. Likewise, the Sr-, Sr-, Sc-, Y-, Dy-, Mg-, Hf- and Ca-doped ceria were prepared and tested toward WS reaction by Meng et al. [38]. Bhosale et al. [39] developed and tested Hf4+ and Zr4+doped ceria toward the thermochemical CS reaction. Recently, Takalkar et al. [40, 41] examined multiple transition metals and lanthanides as the potential dopants for the ceria.

The results reported in the previous studies mainly show that the doped ceria possesses better fuel production capacity as compared to the undoped ceria. To explore further, this investigation reports the utilization of metal cations from the alkali (Li), alkaline earth (Mg, Ca, Sr, Ba), and post-transition (Sn) section of the periodic table as the possible dopants for the ceria material. In previous studies [38, 42, 43], the Mg, Ca, Sr, and Li-doped ceria materials were explored for the WS application; however, their utilization toward CS is not investigated. Furthermore, the Sn-doped ceria was considered for the CS application [44]; nevertheless, the molar concentration of the dopant was 20%. This study reports the utilization of Li-, Mg-, Ca-, Sr-, Ba-, and Sn-doped ceria (Ce0.9 A0.1O2−δ, where A = dopant) for the thermochemical splitting of CO2.

### Experimental section

#### Material preparation and characterization

The synthesis of Ce0.9A0.1O2−δ materials was carried out by using a co-precipitation of the hydroxide method. The metal nitrates and an aqueous solution of ammonium hydroxide (28% NH4OH) were acquired from Sigma-Aldrich and utilized during the synthesis step without any pre-treatment. Deionized water was used for the dissolution of metal nitrates. Ultrapure Inert Ar (purity = 99.999%) needed as a carrier gas, and a gas mixture containing 50%CO2 and 50%Ar (utilized as the reactive gas) were procured from Buzwair Scientific and Technical Gases, Doha, Qatar.

The dopant amounts required for the synthesis of Ce0.9A0.1O2−δ materials (basis 1 g) were controlled by estimating them based on the mole balance. The calculated amounts of metal nitrates were dissolved in 300 ml of deionized water at room temperature. Once the salts were dissolved entirely in deionized water, aqueous ammonium hydroxide was added to the solution in a dropwise manner (to attain a pH of the solution ~ 10). The mixture was agitated for 24 h with a sustained pH ~ 10. During the continuous stirring, due to precipitation, the color of the solution changes from colorless (at time = 0 h) to pale yellow (at time = 24 h). The next day, the stirring was stopped, and the solution obtained was kept undisturbed for 24 h allowing the precipitate to settle at the bottom of the beaker. The precipitated solids were recovered by decanting the supernatant liquid. The solids obtained were washed with water (using a vacuum filtration unit) to eliminate the unreacted chemicals. The solids obtained after vacuum filtration was dried at 120 °C for 5 h. The powder obtained after drying was crushed and annealed up to 1000 °C in the air for 4 h. Before conducting the TGA experiments, the calcined powder of Ce0.9A0.1O2−δ materials was analyzed by using the following techniques:

1. **Synthesis of Ce0.9A0.1O2−δ**
   - **Materials**
     - **Cerium oxide (Ce2O3)**
     - **Ammonium hydroxide (NH4OH)**
     - **Deionized water**
     - **Argon (Ar)**
     - **Carbon dioxide (CO2)**
   - **Methods**
     - **Co-precipitation**

2. **Characterization**
   - **Techniques**
     - **X-ray diffraction (XRD)**
     - **Scanning electron microscopy (SEM)**
     - **Energy dispersive X-ray spectroscopy (EDS)**
     - **Transmission electron microscopy (TEM)**
     - **Thermogravimetric analysis (TGA)**

3. **Results**
   - **Analysis of the synthesized materials**
     - **Phase identification**
     - **Stability and reactivity**
     - **Material properties**

4. **Conclusion**
   - **Summary of findings**
     - **Comparison with previous studies**
     - **Future research directions**
a. Panalytical XPert powder X-ray diffractometer with CuKα radiation (voltage = 45 kV, current = 20 mA, λ = 0.15418 nm.
b. Scanning electron microscope (SEM Nova Nano 450, FEI) equipped with energy-dispersive spectroscopy (EDS)

**Thermogravimetric CS experiments**

Figure 1 shows the SETSYS Evolution thermogravimetric analyzer (TGA) setup used in this investigation. The details associated with the various parts of this setup are already reported in our previous investigations [40, 41]. During the TGA experiments, the graphite heater is protected from the oxidizing gases by utilizing an inert Ar. It was also applied as a carrier gas to avoid probable vapor oxidation of the reactive sample due to gases evolved during the thermochemical reactions. The temperature of the gas streams exiting the TGA setup was controlled and maintained in a safe range by using a continuous flow of chilled water (Julabo FC 1600T). The carrier and protective Ar gas flow rates were measured and monitored continuously with the help of mass flow controllers.

As a starting point of the TGA experiments, ~ 50 mg of Ce0.9A0.1O2−δ powder was placed inside the heating furnace with the help of a platinum (100 µl) crucible. Before each thermochemical experiment, the residual air residing in the hollow space of the furnace was purged with inert Ar. The space of the furnace was then filled with a protective Ar gas with (100 ml/min). The thermal reduction (TR) of the Ce0.9A0.1O2−δ materials was carried out in the presence of inert Ar (at 1400 °C for 60 min), whereas the CS reaction was conducted by utilizing a gas mixture containing 50%CO2 + 50%Ar (at 1000 °C for 30 min). Before analyzing the RR of the Ce0.9A0.1O2−δ materials, a blank TGA experiment was performed by using an empty platinum crucible. The data obtained during the blank experiments were subtracted from the actual TAG experiments (performed by using the Ce0.9A0.1O2−δ materials) to eliminate the thermal buoyancy effect. The mass loss (Δmloss) recorded during each TR step and the mass gain (Δmgain) observed during each CS step was attributed to the nO2 released and nCO produced by each Ce0.9A0.1O2−δ material as follows:

\[
\frac{n_{O_2}}{m_{Ce_{0.9}A_{0.1}O_{2-\delta}}} = \frac{\Delta m_{loss}}{M_{O_2}} \quad (1)
\]

\[
\frac{n_{CO}}{m_{Ce_{0.9}A_{0.1}O_{2-\delta}}} = \frac{\Delta m_{gain}}{M_{O}} \quad (2)
\]

where \(M_{O_2}\) = molecular weight of O2; \(M_{O}\) = molecular weight of O; \(\Delta m_{loss}\) = loss in the mass of Ce0.9A0.1O2−δ (1) recorded during the TR step; \(\Delta m_{gain}\) = gain...
on the mass of Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ recorded during the CS step; $m_{\text{Ce}_{0.9}\text{A}_{0.1}\text{O}_{2-\delta}}$ = total mass of Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ utilized during the TGA experiments.

**Results and discussion**

The synthesized Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials were characterized by using PXRD to identify their phase composition. The wide-angle X-ray diffraction patterns of the co-precipitation synthesized Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials are presented in Fig. 2. Similar to the CeO$_2$, the PXRD peaks of Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials indicate sharp crystalline peaks associated with a cubic fluorite crystal. The PXRD patterns reported in Fig. 2a show the absence of any peaks associated with the metals (Li, Mg, Ca, Sr, Ba, Sn) or individual metal oxides (oxides of Li, Mg, Ca, Sr, Ba, Sn) impurities. The zoomed section of the PXRD ($2\theta = 27^\circ$–$30^\circ$) shows a shift in the peaks for the Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials. Such peak shifts are generally attributed to the replacement of Ce$^{4+}$ cation by another metal cation. Hence, from the shift in the peaks reported in Fig. 2b, it was evident that the Li, Mg, Ca, Sr, Ba, and Sn are successfully incorporated in the CeO$_2$ crystal structure. The formation of Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials was achieved successfully via the co-precipitation of the hydroxide method.

EDS analysis was also performed to explore the elemental composition of Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials. Exemplified EDS plots for Ba- and Sr-doped ceria are reported in Fig. 3. The comparison between the elemental compositions of the as-synthesized and calcined powders and the exact chemical composition of each Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ material is listed in Table 1. The results obtained via the EDS analysis complements the findings associated with the PXRD analysis and confirms the formation of nominally phase pure Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials.

The particle morphology of the Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials was studied via SEM analysis. Exemplified SEM images of CeSr, CeBa, CeCa, and CeSn are presented in Fig. 4. The overall structure of all four images looks very similar, which further indicates

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**Figure 2** PXRD patterns of Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ a $2\theta = 20^\circ$–$90^\circ$, and b $2\theta = 27^\circ$–$30^\circ$.

**Figure 3** Exemplified EDS plots for CeBa and CeSr.
that the doping of different cations, i.e., Li, Mg, Ca, Sr, Ba, and Sn does not have any significant impact on the particle morphology of Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials. The particles are roughly spherical and seem agglomerated. The average particle size for the SEM images obtained was calculated by using the ImageJ software, and it is listed in Table 1. As per the numbers listed, it is evident that all the Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials have an average particle size in the range of 150–200 nm.

Characterized Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials were tested toward thermochemical CS reactions by using a TGA setup. The variations in the mass of the samples were recorded by the Calisto software (embedded in the TGA setup). As an example, a total mass loss of 0.260 mg during the TR step conducted at 1400 °C, and a total mass gain of 0.128 mg during the CS step performed at 1000 °C was recorded for the CeMg material. These mass variations were converted into the $n_{O_2}$ released (163.0 μmol/g) and $n_{CO}$ produced (160.0 μmol/g) by the CeMg materials by using Eqs. (1) and (2). The ratio of $n_{CO}/n_{O_2}$ for CeMg = 0.981 (considerably lower than the theoretical ratio = 2). A similar trend was noticed in the case of other Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials.

A higher release of O$_2$ during the TR step as compared to the lower production of CO during the CS step was unusual. As per the published literature [40, 41], the loss in the mass of reactive samples recorded during the first TR step can be attributed to

### Table 1 Chemical composition of Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ materials: EDS analysis

| Abbreviations | Ce/A ratio (as-prepared) | Ce/A ratio (calcined) | Ce$_{0.9}$A$_{0.1}$O$_{2-\delta}$ (chemical composition) | SEM-based Average Particle Size (nm) |
|---------------|--------------------------|-----------------------|-------------------------------------------------|--------------------------------------|
| CeLi          | 90/10                    | 90.2/10.4             | Ce$_{0.902}$Li$_{0.104}$O$_{1.856}$              | 182.2                                |
| CeMg          | 90/10                    | 89.7/10.6             | Ce$_{0.897}$Mg$_{0.106}$O$_{1.900}$              | 171.4                                |
| CeCa          | 90/10                    | 89.5/9.9              | Ce$_{0.895}$Ca$_{0.099}$O$_{1.889}$              | 179.2                                |
| CeSr          | 90/10                    | 90.4/9.8              | Ce$_{0.904}$Sr$_{0.096}$O$_{1.906}$              | 189.9                                |
| CeBa          | 90/10                    | 89.7/10.2             | Ce$_{0.897}$Ba$_{0.102}$O$_{1.896}$              | 155.1                                |
| CeSn          | 90/10                    | 89.9/10.2             | Ce$_{0.899}$Sn$_{0.102}$O$_{2.002}$              | 163.1                                |

Figure 4 SEM images of
a) CeSr, b) CeBa, c) CeCa, and d) CeSn.
O₂ release plus the release of the volatile components. Some of the chemicals used during the synthesis of the reactive samples remained unburnt during the calcination step (1000 °C). These chemicals were burned and released from the sample during the TR step (1400 °C). By following the results reported in the published literature [40, 41], it was concluded that the nO₂ released by all the Ce₀.₉A₀.₁O₂₋₆ materials, calculated as per the mass loss recorded during the first TR step, was deceptive. Hence, to avoid misrepresentation, the data obtained during the first cycle were not considered hereafter.

The RR of the Ce₀.₉A₀.₁O₂₋₆ materials was examined by performing four consecutive cycles (by excluding cycle 1). The variations in the mass recorded for cycle 2 to cycle 4 are presented in Fig. 5. The mass variations recorded for cycle 2 to cycle 4 were converted into the nO₂ released and nCO produced and reported in Table 2. The Ce₀.₉A₀.₁O₂₋₆ materials first compared with each other based on the nO₂ released in each cycle. The data listed in Table 2 clearly show that the nO₂ released in cycle 2 by all the Ce₀.₉A₀.₁O₂₋₆ materials was higher than that of cycle 3. According to the numbers obtained, the nO₂ released by CeLi, CeMg, CeCa, CeSr, CeBa, and CeSn in cycle 2 was higher by 1.4 µmol/g, 3.2 µmol/g, 1.8 µmol/g, 1.1 µmol/g, 4.2 µmol/g, and 0.7 µmol/g than cycle 3, respectively. Likewise, the nO₂ released by CeLi, CeMg, CeCa, CeSr, CeBa, and CeSn materials in cycle 4 was lower by 2.0 µmol/g, 4.1 µmol/g, 1.7 µmol/g, 1.1 µmol/g, 2.1 µmol/g, and 1.9 µmol/g as compared to cycle 3, respectively. The data reported for the CS steps have a story similar to the TR step. The CO production capacity of the CeLi, CeMg, CeCa, CeSr, CeBa, and CeSn materials was decreased in cycle 4 by 4.7%, 3.3%, 8.9%, 5.5%, 4.5%, and 18.8% as compared to the CO production realized in cycle 2.

The results obtained in four consecutive cycles indicate that the TR and CS ability of all Ce₀.₉A₀.₁O₂₋₆ materials reduced with the rise in the number of thermochemical cycles. Performing four cycles was an initial check, and hence, a detailed analysis of the co-precipitation synthesized Ce₀.₉A₀.₁O₂₋₆ materials (at least by performing ten cycles) was essential. Therefore, the long-term RR of all the Ce₀.₉A₀.₁O₂₋₆ materials was examined by performing a set of 10 consecutive cycles. Again, to avoid the misrepresentation, the data obtained in the first cycle were not considered in this analysis. The TGA profiles obtained for all the Ce₀.₉A₀.₁O₂₋₆ materials from cycle 2 to cycle 10 are presented in Fig. 6. A close look at the TGA plots shows an indication of the attainment of stable RR by the Ce₀.₉A₀.₁O₂₋₆ materials at around cycle 4 to cycle 5. However, a detailed comparison in terms of numbers was a must.

The nO₂ released by the Ce₀.₉A₀.₁O₂₋₆ materials during each thermochemical cycle is presented in Fig. 7. The data presented show that all the Ce₀.₉A₀.₁O₂₋₆ materials indicate a stable release of O₂ from cycle 4 to cycle 10. For example, the CeSr released 60.7 µmol/g, 60.1 µmol/g, 60.8 µmol/g, and 60.4 µmol/g of O₂ in cycle 4, cycle 6, cycle 8, and cycle 10. Likewise, the CeMg is also capable of releasing a stable amount of O₂ in the range of 68.0–68.8 µmol/g from cycle 4 to cycle 10. Similar to the O₂ releasing capacity, the CO production aptitude of all the Ce₀.₉A₀.₁O₂₋₆ materials was also noticed to be steady from cycle 4 to cycle 10 (Fig. 8). For example, CeLi produced 126.3 µmol/g, 126.0 µmol/
g, 126.6 μmol/g, and 125.9 μmol/g of CO in cycles 4, 6, 8, and 10. The results obtained indicate that the initial four cycles were needed to stabilize the material properties and molecular interaction between the cations to achieve a constant O2 release and CO production.

Besides the interaction between the metal cations, the morphology and crystal structure also play a vital role in the stability of the redox materials. The Ce0.9A0.1O2−δ materials obtained after performing the first, fifth, and tenth thermochemical cycles were characterized via SEM and PXRD. The findings acquired via PXRD analysis shows that the phase composition of all Ce0.9A0.1O2−δ materials remained unaffected during multiple thermochemical cycles. The exemplified PXRD peaks for CeMg and CeBa are reported in Fig. 9a, b. The SEM analysis indicates that due to the high-temperature sintering, significant growth in the particle size of Ce0.9A0.1O2−δ materials was recorded after cycle 1. It was also understood that the material morphology of the reacted Ce0.9A0.1O2−δ materials obtained after cycle 5 and cycle 10 was identical to morphology observed after cycle 1. The results obtained via SEM analysis shows that the morphology of all Ce0.9A0.1O2−δ materials was
stable from cycle 2 to cycle 10. As an example, the SEM images for the CeMg and CeBa obtained after cycle 1, cycle 5, and cycle 10 are presented in Fig. 10a, b.

Figure 11 represents the comparison between the Ce_{0.9}A_{0.1}O_{2−δ} materials based on average n_{O2} released, n_{CO} produced, and n_{CO}/n_{O2} ratio (from cycle 2 to cycle 10). In terms of n_{O2} released, the Ce_{0.9}A_{0.1}O_{2−δ} materials can be arranged as: CeSn > CeBa > CeMg > CeLi > CeSr > CeCa. The average n_{O2} released by all the Ce_{0.9}A_{0.1}O_{2−δ} materials was very close to each other. It was observed to be in the range of 60–70 μmol/g cycle, except for CeSn, for which it was considerably higher (107.6 μmol/g cycle). Similar to the average n_{O2} released, the average n_{CO} produced by the CeSn materials (180.5 μmol/g cycle) was relatively higher than the other Ce_{0.9}A_{0.1}O_{2−δ} materials. Based on their average n_{CO} production capacity, the investigated Ce_{0.9}A_{0.1}O_{2−δ} materials can be ranked in the following order: CeSn > CeLi > CeMg > CeSr > CeBa > CeCa. Overall, as presented in Fig. 11, the incorporation of Li, Mg, Ca, Sr, Ba, and Sn has considerably improved the RR of Ce_{0.9}A_{0.1}O_{2−δ} materials as compared to the pure ceria.

The CeSn and CeCa were observed to be the top and bottom-most choices for the CS. Although the CeSn materials seem to the best choice in terms of average n_{O2} released and n_{CO} produced, the average n_{CO}/n_{O2} ratio was considerably lower than most of the Ce_{0.9}A_{0.1}O_{2−δ} materials. As shown in Fig. 11, the Ce_{0.9}A_{0.1}O_{2−δ} materials can be categorized in the following order based on their re-oxidation ability:

CeSr > CeLi ~ CeCa > CeMg > CeSn > CeBa.

These results indicate that the CO production ability for the CeSn can be further increased by improving the n_{CO}/n_{O2} ratio. Our research group is currently exploring the Ce_{x}Sn_{1−x}O_{2−δ} (where x = 0.05–0.5) materials to find out the best candidate for the thermochemical WS and CS.

**Summary and conclusions**

By applying the co-precipitation of the hydroxide method, the Ce_{0.9}A_{0.1}O_{2−δ} materials were synthesized by doping the alkali (Li), alkaline earth (Mg, Ca, Sr, Ba), and post-transition (Sn) metal cations in the ceria cubic structure. The nominally phase pure
composition of each Ce$_{0.9}$A$_{0.1}$O$_{2-d}$ material was confirmed via the PXRD and EDS analysis. The SEM analysis indicates that the doping of different cations, i.e., Li, Mg, Ca, Sr, Ba, and Sn does not have any significant impact on the particle morphology of Ce$_{0.9}$A$_{0.1}$O$_{2-d}$ materials (average particle size in the range of 150–200 nm). The long-term RR of the Ce$_{0.9}$A$_{0.1}$O$_{2-d}$ materials was investigated in ten successive thermochemical cycles. The O$_2$ releasing and CO production capacity of each Ce$_{0.9}$A$_{0.1}$O$_{2-d}$ material were observed to be steady from cycle 4 to cycle 10. In terms of average n$_{O_2}$ released from cycle 2 to cycle 10, the Ce$_{0.9}$A$_{0.1}$O$_{2-d}$ materials can be arranged as: CeSn > CeBa > CeMg > CeLi > CeSr > CeCa. On the other hand, based on their average n$_{CO}$ production capacity from cycle 2 to cycle 10, the investigated Ce$_{0.9}$A$_{0.1}$O$_{2-d}$ materials can be ranked in the following order: CeSn > CeLi > CeMg > CeSr > CeBa > CeCa. CeSn material showed the highest n$_{O_2}$ release (107.6 μmol of O$_2$/g cycle) and n$_{CO}$ production (180.5 μmol of CO/g cycle) as compared to the CeO$_2$ and the remaining Ce$_{0.9}$A$_{0.1}$O$_{2-d}$ 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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