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# Crystal structure and surface characteristics of Sr-doped $\text{GdBaCo}_2\text{O}_{6-\delta}$ double perovskites: oxygen evolution reaction and conductivity†

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A cheap and direct solution towards engineering better catalysts through identification of novel materials is required for a sustainable energy system. Perovskite oxides have emerged as potential candidates to replace the less economically attractive Pt and  $\text{IrO}_2$  water splitting catalysts. In this work, excellent electrical conductivity ( $980 \text{ S cm}^{-1}$ ) was found for the double perovskite of composition  $\text{GdBa}_{0.6}\text{Sr}_{0.4}\text{Co}_2\text{O}_{6-\delta}$  which is consistent with a better oxygen evolution reaction activity with the onset polarisation of 1.51 V with respect to a reversible hydrogen electrode (RHE).  $\text{GdBa}_{1-x}\text{Sr}_x\text{Co}_2\text{O}_{6-\delta}$  with increasing Sr content was found to crystallise in the higher symmetry tetragonal  $P4/mmm$  space group in comparison with the undoped  $\text{GdBaCo}_2\text{O}_{6-\delta}$  which is orthorhombic ( $Pmmm$ ), and yields higher oxygen uptake, accompanied by higher Co oxidation states. This outstanding electrochemical performance is explained by the wider carrier bandwidth, which is a function of Co–O–Co buckling angles and Co–O bond lengths. Furthermore the higher oxygen evolution activity was observed despite the formation of non-lattice oxides (mainly hydroxide species) and enrichment of alkaline earth ions on the surface.

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## 1. Introduction

Single layered perovskites ( $\text{ABO}_{3-x}$ ; A = rare earth and alkaline earth, B = transition metal) have been well documented as excellent intermediate temperature ( $\sim 600$  to  $800 \text{ }^\circ\text{C}$ ) solid oxide fuel cell (SOFC) cathodes due to their high oxygen surface exchange, and excellent ionic and electronic conductivity.<sup>1–7</sup> Interestingly, this class of material can also perform as an oxygen evolution catalyst.<sup>8–11</sup> More recently, transformation of single perovskites with randomly occupied A site into ordered perovskites ( $\text{AA}'\text{BB}'\text{O}_{6-\delta}$ ; A = rare earth, A' = alkaline earth, B and B' = transition metals) has shown improved oxygen transport properties and may potentially replace the conventional

single layered perovskites for a range of technological applications.<sup>12–14</sup> Whilst the oxygen evolution yield of double perovskites is scarcely documented, Grimaud *et al.*,<sup>15</sup> Wu *et al.*<sup>16</sup> and Zhao *et al.*<sup>17</sup> reported the prospect of  $(\text{ABa})\text{Co}_2\text{O}_{6-\delta}$  (A = Pr, Sm, Gd and Ho) and  $\text{PrBa}_{1-x}\text{Sr}_x\text{Co}_2\text{O}_{6-\delta}$  and  $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{6-\delta}$ , respectively to become active catalysts for water oxidation in alkaline solution. This was postulated to be related to the filling of 3d  $e_g$  orbital occupancy to unity and to the location of the oxygen p-band with respect to the Fermi level, similar to the band structure found in  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  single perovskite.<sup>9</sup> In addition, Matsumoto *et al.*<sup>8</sup> reported that the  $\sigma^*$  band formation and higher transition metal oxidation state contributed to higher oxygen evolution catalytic activity in perovskite oxides. In another double perovskite system,  $\text{PrBa}_{0.85}\text{Ca}_{0.15}\text{MnFeO}_{6-\delta}$  was stable and catalytically active for both oxygen reduction and evolution reactions.<sup>18</sup>

Double perovskites with the general formula  $\text{AA}'\text{BB}'\text{O}_{6-\delta}$  afford flexibility in the cation coordination environment and thus offer the opportunity to tune the band structure by varying the nominal composition. The stoichiometric  $\delta = 0$  composition leads to the B cation being octahedrally connected to the oxygen ions, whilst  $\text{BO}_5$  square pyramids are formed for  $\delta = 1$  due to the disappearance of the octahedral apical oxygen ion. This oxygen vacancy ordering is directly linked to the A and A' cation occupancies in the unique crystallographic sites along the  $z$  crystallographic axis, leading to doubling in the  $c$  lattice parameter,

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when compared to the parent single perovskite. This cation ordering varies with temperature and A/A' ionic radii.<sup>19,20</sup> Three commonly reported crystal structure configurations for AA'B<sub>2</sub>O<sub>6-δ</sub> (A = Gd, A' = Ba and B = Co) are presented in Fig. 1: tetragonal *P4/mmm*, orthorhombic *Pmmm* (formula unit per unit cell, *Z* = 1) and *Pmmm* (*Z* = 2) space groups. The difference between the last two structure types is that where *Z* = 2 there is further ordering in the *y* crystallographic axis, in addition to *z*, whilst for *Z* = 1, only ordering in *z* is observed. The oxygen vacancies in these ordered double perovskites were often reported to lie in the rare-earth layers hence lowering the coordination number from 12 to 8 for the smaller rare-earth ions and keeping the same coordination for the larger alkaline earth metals.<sup>21,22</sup> This influences oxide ion migration where fast diffusion pathways were found to be in the *ab* planes in the ordered structure, as predicted by molecular dynamics simulation, rather than isotropic conduction in three dimensions in the disordered single perovskite phase.<sup>12</sup> Thus, oriented samples in the form of either single crystals or epitaxially grown films will enhance the observation of this anisotropic behaviour.

Depending on the oxygen stoichiometry, GdBaCo<sub>2</sub>O<sub>6-δ</sub> single crystals were reported to crystallise in the tetragonal ( $0 < \delta < 0.40$ ), orthorhombic with doubling along *b* ( $Z = 2$ ;  $0.40 < \delta < 0.55$ ) and back to tetragonal symmetry ( $0.55 < \delta \leq 1$ ) at room temperature (RT).<sup>23</sup> However, using RT powder X-ray diffraction (XRD), Roy *et al.*<sup>24</sup> described the GdBaCo<sub>2</sub>O<sub>5.45</sub> using *Pmmm* space group (*Z* = 2) whilst *Pmmm* (*Z* = 1) for GdBaCo<sub>2</sub>O<sub>5</sub>. Introduction of a Sr dopant into the Ba lattice site in GdBa<sub>1-x</sub>Sr<sub>x</sub>Co<sub>2</sub>O<sub>6-δ</sub> leads to the higher symmetry tetragonal *P4/mmm* structure ( $0.2 \leq x \leq 0.6$ ) with another transformation to a structure with *Pnma* symmetry observed as Ba was fully substituted by Sr (GdSrCo<sub>2</sub>O<sub>6</sub>).<sup>25</sup> Higher Sr dopant in PrBa<sub>1-x</sub>Sr<sub>x</sub>Co<sub>2</sub>O<sub>6-δ</sub> led to better oxygen evolution activity with the highest reported for the PrBa<sub>0.25</sub>Sr<sub>0.75</sub>Co<sub>2</sub>O<sub>6-δ</sub> composition.<sup>16</sup> The complex ordering in this type of perovskite as a function of oxygen content, temperature and dopant level has resulted in various space groups being reported, although the correlation between crystal structure and electrochemical performance has rarely been probed.

The bulk chemistry and structure explained previously is often different from the surface, defined as the interface between gas-

solid phase. Lee *et al.*<sup>26</sup> reported that the surface segregation on perovskite oxides was mainly driven by the elastic and electrostatic interactions. As oxygen reduction and evolution reactions between the gas phase and ions primarily occurs at the surface, the surface characteristics are unequivocally required to be understood. Using low energy ion scattering (LEIS),<sup>27,28</sup> which is sensitive to the atomic composition at the outermost surface, Sr and Ba were found to segregate to the surface in polished pellets (subjected to annealing at 1000 °C for 12 h in 200 mbar O<sub>2</sub>) of polycrystalline La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> and GdBaCo<sub>2</sub>O<sub>6-δ</sub>, respectively with transition metal enrichment in the sub-surface region (2–10 nm).<sup>29,30</sup> In this work, we investigate the chemical and electronic speciation at the surface of strontium doped GdBaCo<sub>2</sub>O<sub>6-δ</sub> double perovskites and relate these with the bulk composition, crystal structure, and electrochemical properties.

## 2. Experimental methods

### 2.1. Synthesis

Powders with nominal compositions of GdBa<sub>1-x</sub>Sr<sub>x</sub>Co<sub>2</sub>O<sub>6-δ</sub> (*x* = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) were synthesised using the solid state reaction of Gd<sub>2</sub>O<sub>3</sub> (Alfa Aesar, 99.99%), BaCO<sub>3</sub> (Alfa Aesar, 99.8%), SrCO<sub>3</sub> (Alfa Aesar, 99.99%) and Co<sub>3</sub>O<sub>4</sub> (Alfa Aesar, 99.7%). Stoichiometric amounts of starting powders were manually ground in an agate mortar, sintered at 1100 °C for 60 h in static air in alumina crucibles with intermediate grinding without any pre-calcination step.

### 2.2. Characterisation methods

The oxygen content calculated from the oxidation state of cobalt was determined using iodometric titration. ~70 mg of sample was dissolved in 20 ml hydrochloric acid (12 M) by stirring in an argon gas flushed flask, covered by 0.1 M KI. 0.01 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was used to titrate the iodine generated with starch used as an indicator.

Laboratory powder X-ray diffraction (XRD) patterns were collected at room temperature from 10–120° 2θ using a PANalytical X'Pert Pro MPD utilising CuK<sub>α</sub> source radiation ( $\lambda_{\text{average}} = 1.54 \text{ \AA}$ ) with a step size of 0.016° and accumulating for 0.8 s per step. The crystal structures of GdBa<sub>1-x</sub>Sr<sub>x</sub>Co<sub>2</sub>O<sub>6-δ</sub> were refined by

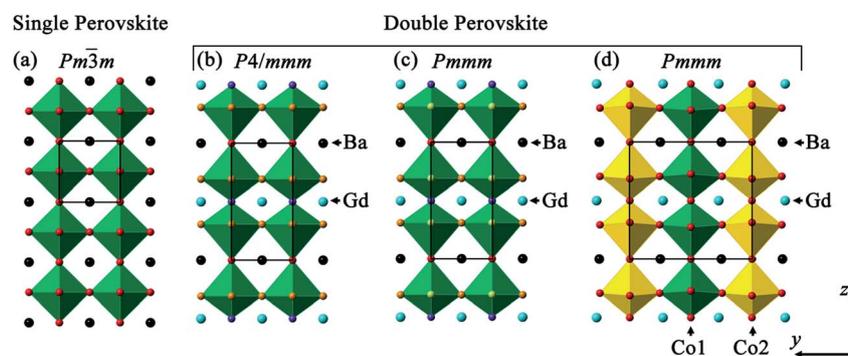


Fig. 1 Crystal structure representation of (a) single ABO<sub>3</sub> perovskite where A is represented in black and BO<sub>6</sub> polyhedra in green; and (b–d) double perovskite GdBaCo<sub>2</sub>O<sub>6</sub> where Gd<sup>3+</sup> (blue) and Ba<sup>2+</sup> cations (black) are ordered in *z* direction with (b) tetragonal *P4/mmm*, (c) orthorhombic *Pmmm* and (d) *Pmmm* with additional ordered cations along *b* depicted by Co1O<sub>6</sub> (green) and Co2O<sub>6</sub> (yellow) octahedra ordering.



Table 1 Chemical composition determined by electron probe microanalysis

Label	Description	Nominal composition	Measured composition
GBCO	As polished	GdBaCo <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.04(1)</sub> Ba <sub>1.01(2)</sub> Co <sub>1.95(1)</sub> O <sub>6-δ</sub>
GBCO-600C	Polished and heat-treated at 600 °C	GdBaCo <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.02(4)</sub> Ba <sub>1.01(2)</sub> Co <sub>1.96(3)</sub> O <sub>6-δ</sub>
GBCO-800C	Polished and heat-treated at 800 °C	GdBaCo <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.03(2)</sub> Ba <sub>1.00(1)</sub> Co <sub>1.98(3)</sub> O <sub>6-δ</sub>
GB8S2CO	As polished	GdBa <sub>0.8</sub> Sr <sub>0.2</sub> Co <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.01(2)</sub> Ba <sub>0.82(2)</sub> Sr <sub>0.20(2)</sub> Co <sub>1.97(3)</sub> O <sub>6-δ</sub>
GB8S2CO-600C	Polished and heat-treated at 600 °C	GdBa <sub>0.8</sub> Sr <sub>0.2</sub> Co <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.02(2)</sub> Ba <sub>0.81(2)</sub> Sr <sub>0.19(2)</sub> Co <sub>1.97(2)</sub> O <sub>6-δ</sub>
GB8S2CO-800C	Polished and heat-treated at 800 °C	GdBa <sub>0.8</sub> Sr <sub>0.2</sub> Co <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.02(3)</sub> Ba <sub>0.80(2)</sub> Sr <sub>0.20(2)</sub> Co <sub>1.98(2)</sub> O <sub>6-δ</sub>
GB7S3CO	As polished	GdBa <sub>0.7</sub> Sr <sub>0.3</sub> Co <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.01(2)</sub> Ba <sub>0.71(3)</sub> Sr <sub>0.28(5)</sub> Co <sub>1.99(5)</sub> O <sub>6-δ</sub>
GB7S3CO-600C	Polished and heat-treated at 600 °C	GdBa <sub>0.7</sub> Sr <sub>0.3</sub> Co <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.01(2)</sub> Ba <sub>0.71(2)</sub> Sr <sub>0.29(2)</sub> Co <sub>1.99(2)</sub> O <sub>6-δ</sub>
GB7S3CO-800C	Polished and heat-treated at 800 °C	GdBa <sub>0.7</sub> Sr <sub>0.3</sub> Co <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.02(2)</sub> Ba <sub>0.71(2)</sub> Sr <sub>0.29(2)</sub> Co <sub>1.98(2)</sub> O <sub>6-δ</sub>
GB6S4CO	As polished	GdBa <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.01(3)</sub> Ba <sub>0.62(2)</sub> Sr <sub>0.40(2)</sub> Co <sub>1.97(3)</sub> O <sub>6-δ</sub>
GB6S4CO-600C	Polished and heat-treated at 600 °C	GdBa <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.02(2)</sub> Ba <sub>0.61(2)</sub> Sr <sub>0.39(3)</sub> Co <sub>1.98(2)</sub> O <sub>6-δ</sub>
GB6S4CO-800C	Polished and heat-treated at 800 °C	GdBa <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>2</sub> O <sub>6-δ</sub>	Gd <sub>1.02(2)</sub> Ba <sub>0.61(3)</sub> Sr <sub>0.39(4)</sub> Co <sub>1.98(4)</sub> O <sub>6-δ</sub>

Rietveld analysis<sup>31,32</sup> using a fundamental parameter peak shape profile<sup>33</sup> implemented in TOPAS Version 4.1.<sup>34</sup> The starting models used the *P4/mmm*,<sup>19</sup> *Pmmm* ( $Z = 1$ )<sup>19</sup> and *Pmmm* ( $Z = 2$ )<sup>35</sup> atomic positions of GdBaCo<sub>2</sub>O<sub>6-δ</sub> with Sr occupying the same site as Ba. For each data set, a five-coefficient Chebyshev polynomial and  $1/x$  background, a zero error, unit-cell parameters, scale factors and crystal size were refined sequentially. X-ray form factors for Gd<sup>3+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Co<sup>3+</sup> and O<sup>2-</sup> were used.

Samples for low energy ion scattering (LEIS), collected using Qtac100 spectrometer, IonTOF GmbH, Germany, were uniaxially pressed, and followed by sintering at 1100 °C for 12 h. The achieved density was 85–95% of theoretical density, measured by the Archimedes method. The pellets were polished to a final particle size of 1/4 μm and subjected to subsequent heat treatment annealing at 600 °C and 800 °C for 12 h in static air. The sample labelling is listed in Table 1. The primary beam used was 5 keV Ne<sup>+</sup> normal to the surface with the collection angle of 145° with an analysis area of 500 μm × 500 μm whilst the sputter beam of 0.5 keV Ar<sup>+</sup> ions at 59° incidence angle was utilised with a sputter area of 1000 μm × 1000 μm. The larger sputter area ensures that the analysis area is within the sputtered area. The spectra were fitted using SurfaceLab 6 software (IonTOF GmbH, Germany) with Gaussian peaks of different elemental components with the in-depth signal described by error functions.<sup>36,37</sup> The estimated depth was calibrated using interferometric (Zygo NewView 200 interferometer) measurement and the assumption of a constant sputter rate throughout the analysis was made.

The average bulk chemical quantification of the samples used for LEIS analysis over 30–40 data points was determined using electron probe microanalysis (EPMA) in a JEOL JXA-8530F instrument equipped with five wavelength-dispersive spectrometers (WDS). The surface was carbon coated to minimise the effect of charging. The accelerating voltage and current used were 15 kV and 20 nA, respectively. Standards of gadolinium metal (Gd), BaSO<sub>4</sub> (Ba), SrSO<sub>4</sub> (Sr) and cobalt metal (Co), obtained from Astimex, were employed. The peak, low background and high background counting time were 20 s, 10 s and 10 s, respectively.

The pellets were fractured in a glove bag under N<sub>2</sub> atmosphere to minimise exposure to air and moisture. The exposed

fresh pellet surface was characterised using X-ray photoelectron spectroscopy (XPS). The spectra were recorded on a Thermo Scientific K-Alpha<sup>+</sup> X-ray photoelectron spectrometer system operating at  $2 \times 10^{-9}$  mbar base pressure. This system incorporates a monochromated, microfocused Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV) and a 180° double focusing hemispherical analyser with a 2D detector. The X-ray source was operated at 6 mA emission current and 12 kV anode bias and a flood gun was used to minimise sample charging. Data were collected at 20 eV pass energy for core level spectra (Ba 4d, Ba 3d, Gd 4d, Sr 3d, Co 2p, O 1s and C 1s), and at 15 eV pass energy for valence band spectra using an X-ray spot size of 400 μm<sup>2</sup>. All data were analysed using the Thermo Scientific Avantage software package.

### 2.3. Electrochemistry measurement

The total direct current (DC) conductivity was measured by a standard four-point probe method using a Solartron Modulab on a uniaxially pressed rectangular block (33 mm × 4 mm × 4 mm) sintered at 1100 °C (~85 to 95% theoretical density). Silver paint was used as a contact with Ag wires. The measurement was conducted under ambient conditions and a DC current of 200 mA was applied.

Double perovskite catalyst inks were prepared by mixing 2 mg of the as-synthesised catalyst, 0.1 ml propan-2-ol (Fisher,

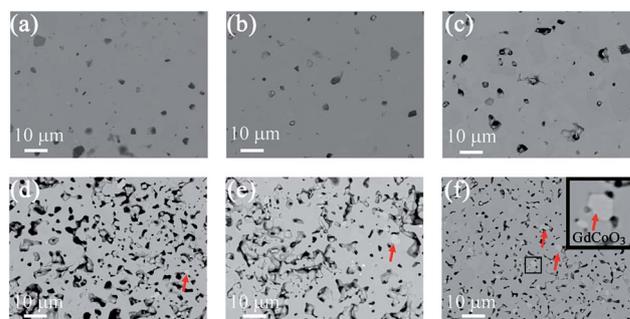


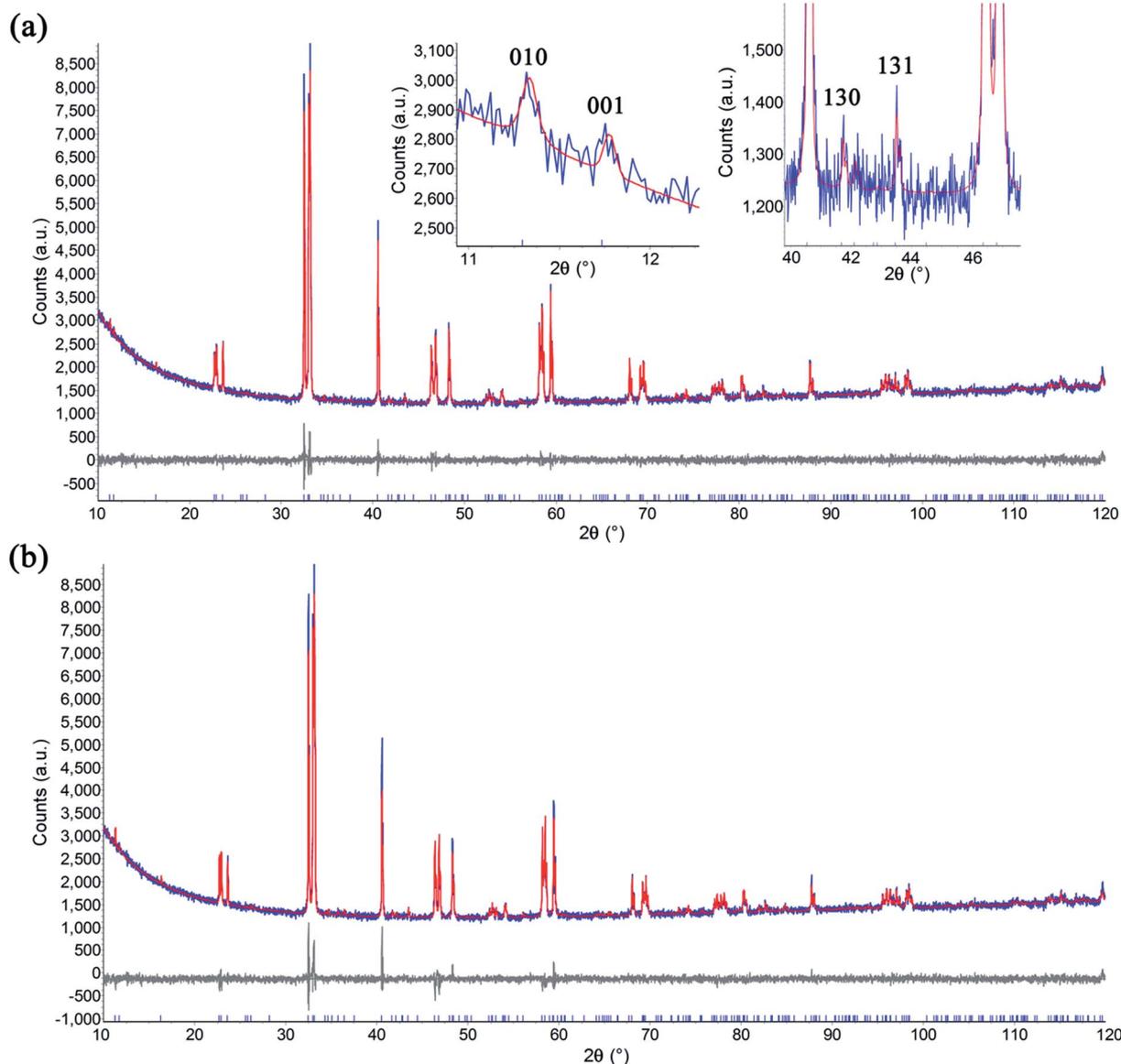
Fig. 2 Back-scattered electron (BSE) images of (a) GBCO, (b) GBCO-600C, (c) GBCO-800C, (d) GB7S3CO, (e) GB7S3CO-600C, (f) GB7S3CO-800C with an inset of enlarged area within the box. Brighter regions marked by red arrows were quantified as a single perovskite Gd<sub>1.00(3)</sub>Co<sub>0.97(3)</sub>O<sub>3</sub> phase.



Analytical Reagent), 0.4 ml deionised H<sub>2</sub>O (Barnstead,  $\geq$  18.2 M $\Omega$  cm) and 60  $\mu$ L of Nafion 117 solution (Sigma Aldrich). The suspensions were sonicated at 20 °C for 30 minutes to ensure homogeneous mixing. 5  $\mu$ L of the catalyst ink was then drop-cast onto polished glassy carbon electrodes (3 mm diameter, CH Instruments). 17.9  $\mu$ g of catalyst was typically loaded

**Table 2** Refined lattice parameters and oxygen content determined from XRD data and iodometric titration respectively for GdBa<sub>1-x</sub>Sr<sub>x</sub>Co<sub>2</sub>O<sub>6- $\delta$</sub>

Compositions	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Volume (Å <sup>3</sup> )	Oxygen content (6 - $\delta$ )
GBCO	<i>Pmmm</i>	3.87844(7)	7.8279(2)	7.5350(1)	228.763(8)	5.21(1)
GB9S1CO	<i>Pmmm</i>	3.87015(5)	7.8065(1)	7.53891(8)	227.769(6)	5.28(1)
GB8S2CO	<i>Pmmm</i>	3.8685(1)	3.8833(1)	7.5421(2)	113.300(6)	5.38(1)
GB7S3CO	<i>Pmmm</i>	3.8634(1)	3.8673(1)	7.5454(2)	112.735(6)	5.51(1)
GB6S4CO	<i>P4/mmm</i>	3.8580(1)	= <i>a</i>	7.5429(2)	112.270(7)	5.54(1)
GB5S5CO	<i>P4/mmm</i>	3.8512(1)	= <i>a</i>	7.5376(2)	111.794(7)	5.55(1)



**Fig. 3** Rietveld plot of the XRD data of GBCO collected at room temperature, (a) with ( $R_{wp} = 0.029$ ,  $R_{Bragg} = 0.007$ ) and (b) without ( $R_{wp} = 0.033$ ,  $R_{Bragg} = 0.020$ ) preferred orientation and anisotropic peak broadening correction. The existence of 010, 130 and 131 reflections at  $2\theta = 11.29$ ,  $41.69$  and  $43.46^\circ$  signify the doubling in *b* (inset). The observed and calculated intensity are shown by blue and red line, respectively, with the differences plotted beneath. Vertical markers indicate the Bragg reflections.



onto each electrode. The electrochemical measurements were performed in a glass H-cell separated with a porous glass plug in the 3-electrode configuration without rotation. A Hg/HgO (in 0.1 M KOH) electrode (CH Instruments) and a platinum wire were used respectively as reference and counter electrodes. The electrolyte was a 0.1 M KOH solution (Alfa Aesar, 99.98%). The reference was calibrated against RHE (Hydroflex, Gaskatel GmbH) in the same electrolyte. A Gamry Reference 600 potentiostat was used to control and measure potentials/currents. A real-time current interrupt iR drop compensation was applied to the measurements. All current densities were normalised to the geometric surface area of the working electrode.

### 3. Results and discussion

#### 3.1. Bulk composition and crystal structure

The average bulk composition of double perovskites measured using electron probe microanalysis, within an 800 nm interaction volume as calculated by Monte Carlo simulation of electron trajectory in solids (Casino),<sup>38</sup> is close to the nominal composition within the standard deviation (Table 1). However, a closer inspection of backscattered electron images shows that there are brighter regions which were quantified to be a single perovskite of composition  $\text{Gd}_{1.00(3)}\text{Co}_{0.97(3)}\text{O}_3$  (Fig. 2 and S1†) and the area density of this secondary phase was more pronounced as the nominal Sr content in the GBCO crystal increased. The oxygen content, determined from iodometric titration, increased from 5.21(1) to 5.55(1) as the nominal Sr dopant level increased from GBCO ( $x = 0$ ) to GB5S5CO ( $x = 0.5$ ) (Table 2).

In order to understand the crystal structure of these double perovskite phases, Rietveld refinement was performed on powder XRD patterns.<sup>31,32</sup> The GBCO sample was found to crystallise in the  $Pm\bar{m}m$  space group ( $Z = 2$ ) with  $a = 3.87844(7)$  Å,  $b = 7.8279(2)$  Å,  $c = 7.5350(1)$  Å. The doubling in  $c$  shows that the ordered double perovskite was successfully synthesised ( $2\theta_{001} = 11.74^\circ$ ) (Fig. 3). In addition, the  $b$  lattice parameter was also doubled, as indicated by the presence of the (010) reflection at  $2\theta = 11.29^\circ$ , in addition to other minor reflections such as (130) and (131) at  $2\theta = 41.69$  and  $43.46^\circ$  respectively. This discounted the possibility of either the  $P4/m\bar{m}m$  or  $Pm\bar{m}m$  ( $Z = 1$ ) space groups existing. Introducing preferred orientation and anisotropic peak broadening corrections led to the reliability factors of  $R_{\text{wp}} = 0.029$  and  $R_{\text{Bragg}} = 0.007$ .

Introducing 10 at% of Sr to the Ba site (GB9S1CO) did not change the symmetry (Fig. S2†). However, the addition of 20 at% Sr (GB8S2CO) diminished the ordering along the  $y$  crystallographic axis, yielding a structure that adopted the  $Pm\bar{m}m$  space group with  $Z = 1$  ( $a = 3.8685(1)$  Å,  $b = 3.8833(1)$  Å,  $c = 7.5421(2)$ ) whilst retaining the  $z$  ordering. Tetragonal  $P4/m\bar{m}m$  was discounted because the (200) reflection ( $2\theta = 47^\circ$ ) was observed to split into two peaks, assigned as (200) and (020), leading to an orthorhombic  $Pm\bar{m}m$  space group assignment (Fig. S3,†  $R_{\text{wp}} = 0.028$ ,  $R_{\text{Bragg}} = 0.005$ ). This was accompanied by the formation of 0.9(2) wt% single perovskite  $\text{GdCoO}_3$  phase, consistent with the EPMA results and the back scattering electron (BSE) micrographs. GB7S3CO crystallised with the same space group as GB8S2CO (Fig. S4†). GB6S4CO and GB5S5CO, however, could be

indexed with a tetragonal structure ( $P4/m\bar{m}m$  space group) verified by the presence of a single (200) reflection. The impurity of  $\text{GdCoO}_3$  increased to 3.0(3) wt% for GB5S5CO as Sr substituted onto the Ba lattice site. Overall, the  $a$ ,  $b$  and unit cell volume decreased as a function of Sr content as the ionic radius of  $\text{Sr}^{2+}$  in 12 coordination (1.44 Å) is smaller than that of  $\text{Ba}^{2+}$  (1.61 Å).<sup>39</sup> In contrast,  $c$  shows an anomaly which increased slightly up to GB7S3CO and decreased as Sr level increased (Fig. 4).

The average equatorial bond lengths of Co–O ((i)  $Pm\bar{m}m$ ,  $Z = 2$ : Co1–O6,7 and Co2–O5,7, (ii)  $Pm\bar{m}m$ ,  $Z = 1$ : Co1–O2,3, (iii)  $P4/m\bar{m}m$ : Co1–O2) are relatively constant for GBCO, GB9S1CO and GB8S2CO, whilst with further increase in Sr content, a decrease in equatorial bond length was observed, in agreement with the smaller ionic radius of  $\text{Sr}^{2+}$  (Fig. S7a†). An interesting observation is that the axial Co–O bond length in the Ba plane increased slightly when  $\text{Sr} \geq 40$  at%. Bond valence sum (BVS) analysis,<sup>40,41</sup> which indicates the bond strength in ionic compounds, was calculated taking into account the vacancy in the oxygen site that is located on the Gd plane ( $z = 0.5$ ). For all compounds the BVS of cobalt was found to be in good agreement with the oxidation state obtained from the iodometric titrations (Tables S7–S9†).

#### 3.2. Surface electronic structure and chemistry

The freshly fractured surfaces of GBCO, GB8S2CO, GB7S3CO, and GB6S4CO pellets were characterised using XPS. A consistent trend in the Ba and Sr core level intensities was found

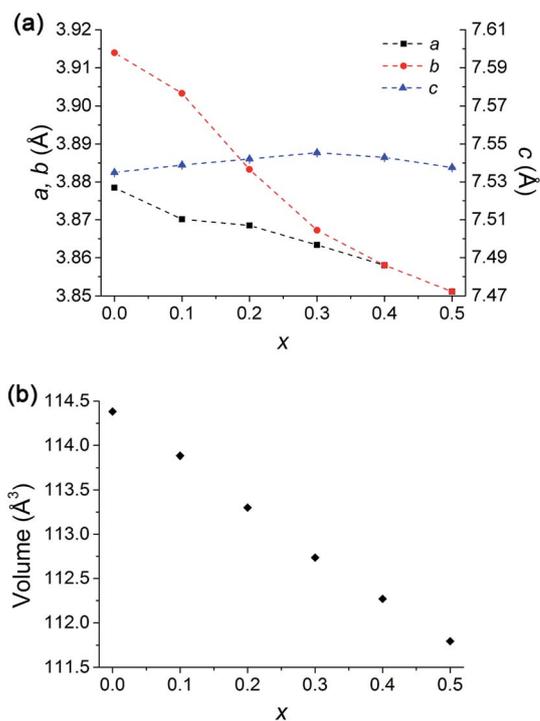


Fig. 4 (a) Lattice parameters of  $\text{GdBa}_{1-x}\text{Sr}_x\text{Co}_2\text{O}_{6-\delta}$  showing a decrease in  $a$  and  $b$  (for  $x = 0$  and 0.1,  $1/2b$  is used for comparison) parameters with increasing Sr dopant whilst  $c$  increases to  $x = 0.3$  and decreases with  $x > 0.3$ . Dashed lines are plotted as a guide to the eye. (b) Volume decreases as  $x$  increases consistent with smaller ionic radius of  $\text{Sr}^{2+}$  than  $\text{Ba}^{2+}$ . Error bars are smaller than the symbols. Note transition to tetragonal at  $x = 0.4$ .







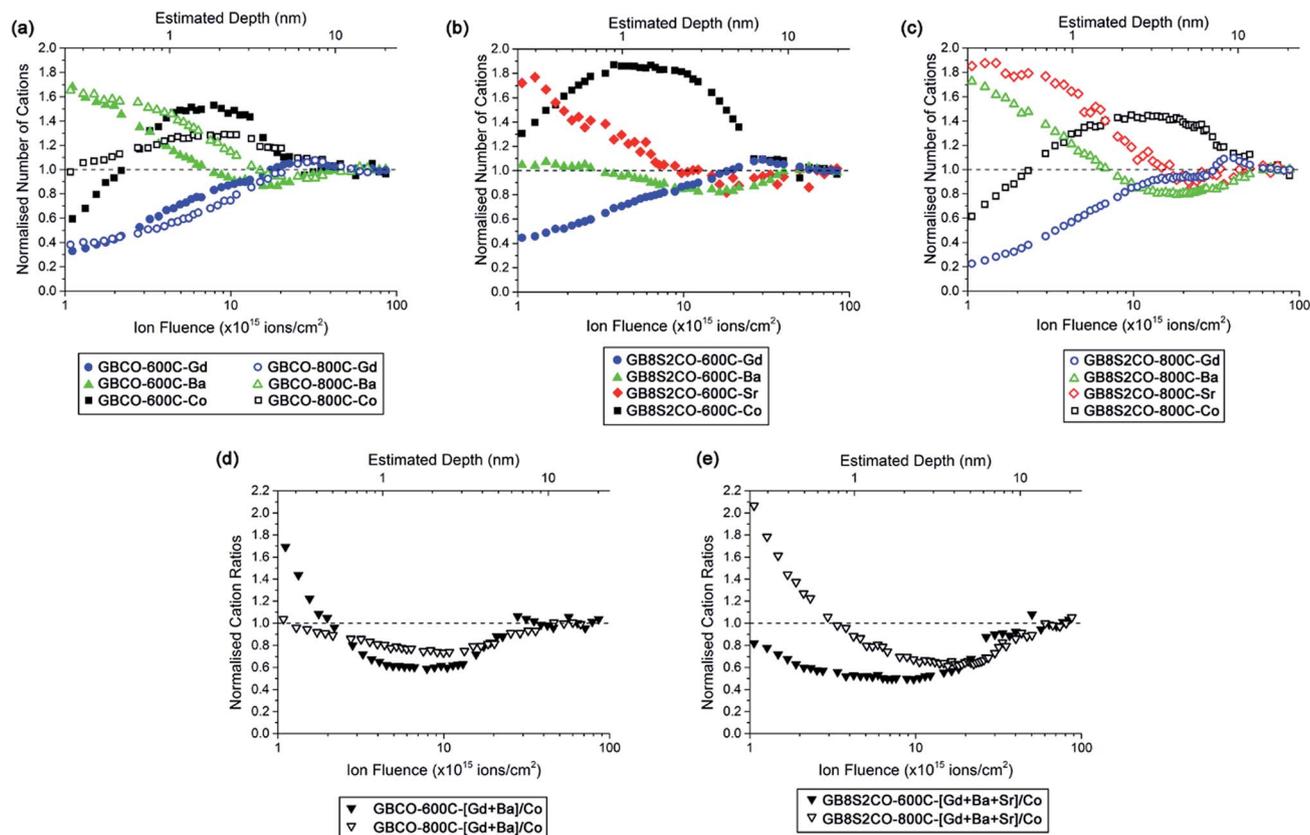


Fig. 7 Cation depth profiles obtained from low energy ion scattering (LEIS) spectroscopy (a) individual cations in GBCO, (b) individual cations in GB8S2CO annealed at 600 °C and (c) individual cations in GB8S2CO annealed at 800 °C, whilst (d, e) [Gd + Ba + Sr]/Co ratio in GBCO and GB8S2CO, respectively.

published report on the segregation behaviour of  $\text{La}_{0.8}(\text{Ca}, \text{Sr}, \text{Ba})_{0.2}\text{MnO}_3$  shows that Ba tends to segregate to the surface due to a larger dopant size mismatch to the La host.<sup>26</sup> In this work, Sr substitution into the Ba site leads to Sr segregation to the sample surface. Another interesting finding is that in the

near-surface region Co is more enriched for samples annealed at lower temperature. The LEIS spectra for GB7S3CO and GB6S4CO annealed at the same temperatures show similar trends with respect to sputtered ion fluence (Fig. S9<sup>†</sup>). For all Sr-doped GBCO, the [A] to [B] cation ratio for the sample annealed at 800 °C is greater than 600 °C and the sub-surface layer is dominated by Co. The only anomaly is at higher Sr levels (GB6S4CO, Fig. S9c<sup>†</sup>), where the surface Sr content was found to be not heavily enriched for the sample annealed at 600 °C, which requires further investigation.

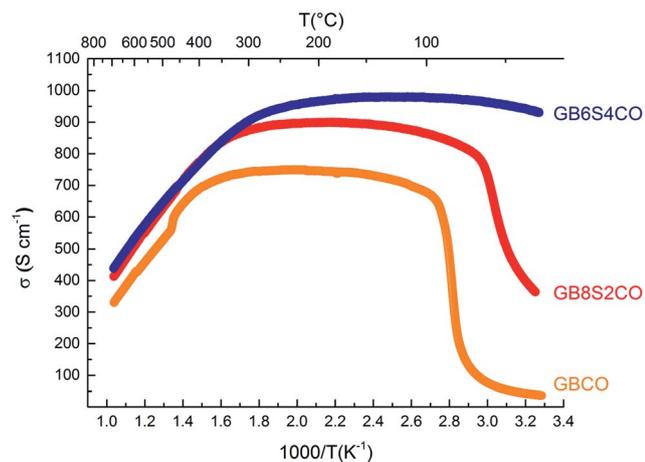


Fig. 8 Total DC electrical conductivity of GBCO (orange), GB8S2CO (red) and GB6S4CO (blue) as a function of temperature showing higher conductivity was achieved for higher Sr-doped sample.

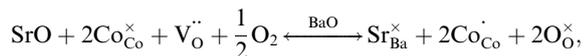
### 3.3. Conductivity and electrochemical performance

In GBCO (relative density of 85%), there are three phase transitions observed, which are at 70 °C, 100 °C and 360 °C with activation energies ( $E_a$ ) typical of a semiconductor (0.19 eV ( $T < 70$  °C), 1.23 eV ( $70$  °C  $< T < 100$  °C) and 0.02 eV ( $100$  °C  $< T < 360$  °C)) (Fig. 8). Above 360 °C, a metallic characteristic is observed. This metallic transition is reported to be accompanied by an orthorhombic  $Pm\bar{3}m$  to tetragonal  $P4/mmm$  phase transition.<sup>55</sup> A sharp electrical conductivity drop at 470 °C is also observed. As Sr replaced Ba, the transition temperature was found to be lower. In GB8S2CO (relative density of 93%),  $E_a$  of 0.22 eV ( $T < 70$  °C) and 0.02 eV ( $70$  °C  $< T < 320$  °C) was observed, whilst  $E_a$  of 0.01 eV ( $T < 250$  °C) was found in GB6S4CO (relative density of 87%).

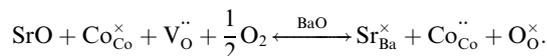


These are followed by a transition to metallic behaviour at temperatures above 320 °C for the former and above 250 °C for the latter. At 130 °C, the conductivity of GB6S4CO reached as high as 980 S cm<sup>-1</sup>, whilst 890 S cm<sup>-1</sup> was obtained for GB8S2CO and 720 S cm<sup>-1</sup> for GBCO. The higher oxygen content, confirmed by iodometric titration, leads to an increase in electronic holes which can be formulated in the Kröger-Vink notation as

Oxidation of Co<sup>2+</sup> to Co<sup>3+</sup> is represented by



whilst Co<sup>2+</sup> to Co<sup>4+</sup> by



Furthermore, when the structure is less distorted (based on consideration of the Goldschmidt tolerance factor<sup>56</sup>) which is close to the ideal cubic perovskite, the conductivity tends to be higher.<sup>25</sup> This is due to a wider charge carrier bandwidth and overlap between Co 3d and O 2p orbitals which is a function of the buckling angle of the Co–O–Co bonds and Co–O bond lengths (Tables S7–S9<sup>†</sup>). Within the tight-binding approximation, the carrier bandwidth ( $w$ ) is given as:<sup>57</sup>

$$w \propto \frac{\left\langle \cos\left(\frac{\pi - \theta_{\text{Co-O-Co}}}{2}\right) \right\rangle}{\langle d_{\text{Co-O}}^{-3.5} \rangle} \quad (1)$$

Combining the effect of average axial and equatorial buckling angles ( $\theta_{\text{Co-O-Co}}$ ) and bond lengths ( $d_{\text{Co-O}}$ ),  $w$  increases with Sr dopant leading to higher electronic conductivity (Fig. S7b<sup>†</sup>), consistent with earlier reports.<sup>58,59</sup>

The onset potential for oxygen evolution in Sr doped GBCO was found to be ~1.50 to 1.52 V with respect to the reversible hydrogen electrode (RHE). This is approximately 50–70 mV earlier than that for the undoped GBCO (1.57 V) as determined by linear sweep voltammetry with scanning rate of 1 mV s<sup>-1</sup> performed on static electrodes (Fig. 9a). No significant improvement in the onset potential was observed as more Sr was introduced; however, a much higher oxygen evolution current density was achieved when GBCO was doped with 40 at% Sr (GB6S4CO). Notably, the Tafel slope also decreased, from close to 100 mV dec<sup>-1</sup> for the undoped GBCO, to around 80 mV dec<sup>-1</sup> for Sr doped GBCO which is closer to the reported 60 mV dec<sup>-1</sup> for (ABa)Co<sub>2</sub>O<sub>6-δ</sub> (A = Pr, Sm, Gd and Ho) in O<sub>2</sub>-saturated 0.1 M KOH electrolyte.<sup>15</sup> The smaller Tafel slope seen in the doped sample indicates a possible shift in the rate limiting step of the oxygen evolution reaction from M–OH formation to M–OO formation or O<sub>2(g)</sub> desorption, where M represents a site on the surface.<sup>60</sup>

We note that the OER activity of this double perovskite is comparable with previously reported LaCoO<sub>3-δ</sub>, better than LaCrO<sub>3-δ</sub> and LaMnO<sub>3-δ</sub> single perovskites, but lower than Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub>.<sup>9</sup> The OER performances of selected double perovskites are listed in Table S10.<sup>†</sup> The higher current

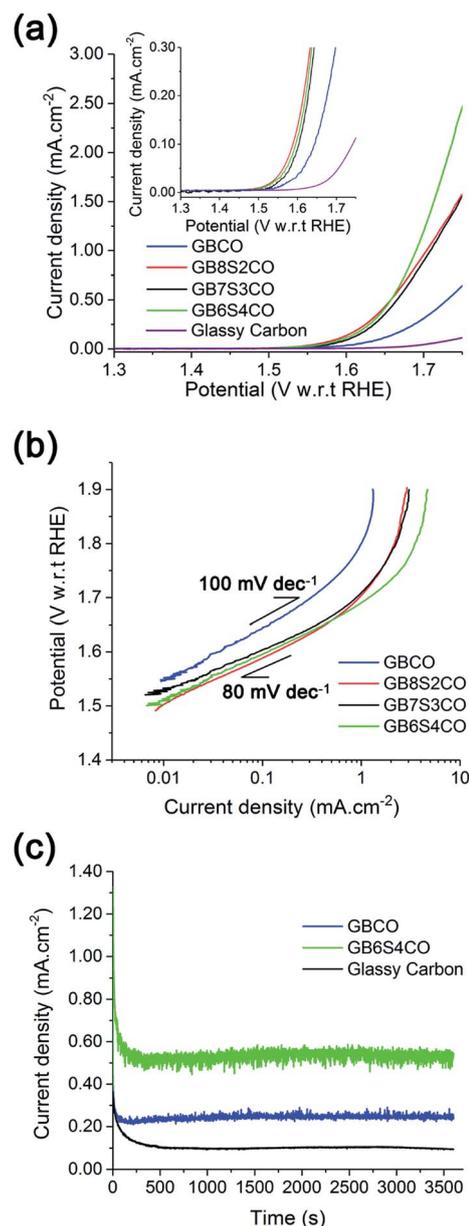


Fig. 9 (a) Linear sweep voltammetry at the 6<sup>th</sup> cycle and the corresponding (b) Tafel plot (at 1 mV s<sup>-1</sup> scan rate) in 0.1 M KOH electrolyte. (c) Chronoamperometry measurements of different GBSCO compounds at 1.65 V ( $\eta = 420$  mV). Electrochemical measurements were iR compensated using current interrupt method. Higher performance was achieved with higher Sr dopant level.

density exhibited by the Sr doped GBCO was also sustainable, as demonstrated by chronoamperometric measurements, with its activity after one hour at 1.65 V ( $\eta = 420$  mV) maintained at 0.53 mA cm<sup>-2</sup>, which is ~2.5 times higher compared to the undoped GBCO (Fig. 9c).

## 4. Conclusions

Strontium-doped double perovskites (GdBa<sub>1-x</sub>Sr<sub>x</sub>Co<sub>2</sub>O<sub>6-δ</sub>) possess improved oxygen evolution catalytic performance and higher electrical conductivity compared to undoped



GdBaCo<sub>2</sub>O<sub>6-δ</sub>. XRD measurements together with Rietveld analysis showed that materials with higher Sr dopant content crystallised with higher symmetry, transforming from orthorhombic *Pmmm* with doubling in *b* and *c* (GBCO and GB9S1CO), transiting to the same *Pmmm* space group with doubling only in *c* (GB8S2CO and GB7S3CO) and finally to tetragonal *P4/mmm* (GB6S4CO and GB5S5CO). This transformation was accompanied by oxygen uptake, lowering the oxygen vacancy content. A combination of higher oxygen concentration, higher Co oxidation state and higher carrier bandwidth (which depends on the Co–O–Co buckling angles and Co–O bond lengths) explains the higher electronic conductivity. The surface enrichment of Ba and Sr, which are mainly in the form of hydroxides, was observed by LEIS and XPS. However, this does not make the surface inactive as shown by higher oxygen evolution current density observed with higher Sr dopant level. Hence, a thorough understanding of the crystallographic occupancy ordering and surface characteristics is essential for optimising the electrical conductivity, ionic mobility and catalytic performance, critical to designing efficient devices.

## Author's contributions

S. S. P. and S. J. S. conceived and designed this work. S. S. P. performed the XRD experiments and analysed the crystal structure of materials. A. C. performed the electrical measurements. S. S. P., A. C., C. L. and J. A. K. carried out the low energy ion scattering spectroscopy measurements and analysed the spectra. R. J. W., A. R. and D. J. P. were involved in the X-ray photoelectron spectroscopy measurements and analyses. Electron probe microanalyses were conducted by S. S. P. and J. S. H.; A. D. H., K. W. C., B. S. Y. and M. P. R. conducted the electrochemistry experiments and analysed the results. All authors co-wrote and reviewed the manuscript.

## Conflicts of interest

There are no conflicts of interest to declare.

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