



Cite this: *EES Catal.*, 2024, 2, 335

## Cobalt-free layered perovskites $\text{RBaCuFeO}_{5+\delta}$ ( $\text{R} = 4\text{f}$ lanthanide) as electrocatalysts for the oxygen evolution reaction<sup>†</sup>

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Co-based perovskite oxides are intensively studied as promising catalysts for electrochemical water splitting in an alkaline environment. However, the increasing Co demand by the battery industry is pushing the search for Co-free alternatives. Here we report a systematic study of the Co-free layered perovskite family  $\text{RBaCuFeO}_{5+\delta}$  ( $\text{R} = 4\text{f}$  lanthanide), where we uncover the existence of clear correlations between electrochemical properties and several physicochemical descriptors. Using a combination of advanced neutron and X-ray synchrotron techniques with *ab initio* DFT calculations we demonstrate and rationalize the positive impact of a large R ionic radius in their oxygen evolution reaction (OER) activity. We also reveal that, in these materials,  $\text{Fe}^{3+}$  is the transition metal cation the most prone to donate electrons. We also show that similar  $\text{R}^{3+}/\text{Ba}^{2+}$  ionic radii favor the incorporation and mobility of oxygen in the layered perovskite structure and increase the number of available O diffusion paths, which have an additional, positive impact on both, the electric conductivity and the OER process. An unexpected result is the observation of a clear surface reconstruction exclusively in oxygen-rich samples ( $\delta > 0$ ), a fact that could be related to their superior OER activity. The encouraging intrinsic OER values obtained for the most active electrocatalyst ( $\text{LaBaCuFeO}_{5.49}$ ), together with the possibility of industrially producing this material in nanocrystalline form should inspire the design of other Co-free oxide catalysts with optimal properties for electrochemical water splitting.

Received 19th June 2023,  
Accepted 30th October 2023

DOI: 10.1039/d3ey00142c

rsc.li/eescatalysis

### Broader context

Co oxides with perovskite-related structure are particularly promising, cost-effective OER catalysts. However, the increasing Co demand by the battery industry is pushing the search for Co-free alternatives. Here we investigate the potential of the Co-free layered perovskite family  $\text{RBaCuFeO}_{5+\delta}$  ( $\text{R} = 4\text{f}$  lanthanide), where we identify the critical structural and electronic variables leading to high OER catalytical performance. The employed methodology, based in the use of advanced neutron and X-ray synchrotron techniques combined with *ab initio* DFT calculations allowed to reveal  $\text{LaBaCuFeO}_{5+\delta}$  as new, promising Co-free electrocatalyst. Moreover, we could show that this material can be industrially produced in nanocrystalline form. We believe that the reported results and methodology may contribute to the implementation of new technologies aimed to generate energy with lower carbon emissions, and can also inspire the scientific community in their search of other Co-free materials with good OER electrocatalytical properties.

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<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3ey00142c>

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## 1. Introduction

The targeted decarbonisation of human activities by 2050 requires the rapid development of green technologies able to generate energy using renewable sources and convert (or store) it to zero-carbon emission carriers. Among them, the use of hydrogen produced by the water-splitting process is considered among the most promising to meet the decarbonisation goal. However, the anodic reaction in water electrolyzers, the oxygen evolution reaction (OER), is a complex process involving a transfer of four electrons that is affected by a slow dynamic (high kinetic overpotential) that controls *de facto* the water splitting efficiency. Perovskite-type oxides with general formula  $\text{ABO}_3$  (henceforth perovskite oxides) are particularly promising for electrocatalysis in alkaline media due to their structural flexibility, which allows accommodating a large variety of cations in the A and B sites and the creation of both, anionic and cationic defects.<sup>1–7</sup> This provides a plethora of possibilities for tailoring their physicochemical properties, which can be effectively tuned to boost the activity of the OER process.<sup>4–6</sup>

In most perovskite oxide catalysts the A-positions are occupied by 4f lanthanides and/or alkaline earth cations, whereas the B positions host cations of abundant transition metals (TM) such as Mn, Fe, Co or Ni.<sup>2,5,8</sup> Among them, Co is particularly well suited for reactions involving electron exchange (such as the OER) due to the close values of their intra-atomic exchange energy  $J_{\text{H}}$  and crystal electric field (CEF) splitting  $10D_{\text{q}}$ , which results in small energy differences between their spin-state and oxidation states.<sup>9–12</sup> The presence of cobalt on the B-sites has indeed emerged as beneficial for the OER process, with Co-based perovskites such as the three-dimensional (3D) cubic oxide  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  or the layered double perovskite  $\text{PrBaCo}_2\text{O}_{5+\delta}$  showing OER activities as good as or even higher than established catalysts.<sup>13</sup>

Despite its outstanding properties for electrochemical water splitting, Co-based perovskites have a few drawbacks, *e.g.*, cobalt toxicity. Also critical is the high Co price linked to the increasing demand by the battery industry, which is driving the search for alternative, Co-free perovskite oxide catalysts. In the recent literature, some Mn, Ni and/or Fe-based 3D perovskites have been found to display good figures of merit.<sup>1,2,14</sup> However, to our best knowledge, Co-free oxides with the layered perovskite structure have not been investigated to date. Interestingly, this structural framework seems to be at the origin of the excellent electrochemical performance and stability reported for layered Co perovskites, seemingly superior to those of their 3D Co-based counterparts.<sup>15</sup> It is thus tempting to investigate whether this trend is also verified in isostructural, Co-free materials.

In this work, we address this question by investigating the layered perovskite family  $\text{RBaCuFeO}_{5+\delta}$  ( $\text{R} = 4\text{f}$  lanthanide). These Co-free materials have recently attracted a lot of attention due to their promise as spin-driven multiferroics for low-power magnetoelectric applications,<sup>16–20</sup> and some of them have also been investigated as potential cathodes for intermediate-temperature solid oxide fuel cells.<sup>21–23</sup> However, they have never

been considered before as OER electrocatalysts as far as we know. Interestingly, their layered perovskite structure<sup>24</sup> is similar to that of  $\text{PrBaCo}_2\text{O}_{5+\delta}$ , one of the most OER-active perovskite-related oxides reported to date. Moreover, the possibility of incorporating the complete 4f lanthanide series in one of the two A-sites provides an attractive, novel possibility for crystal structure and physical property tuning that has no equivalent in 3D perovskites.

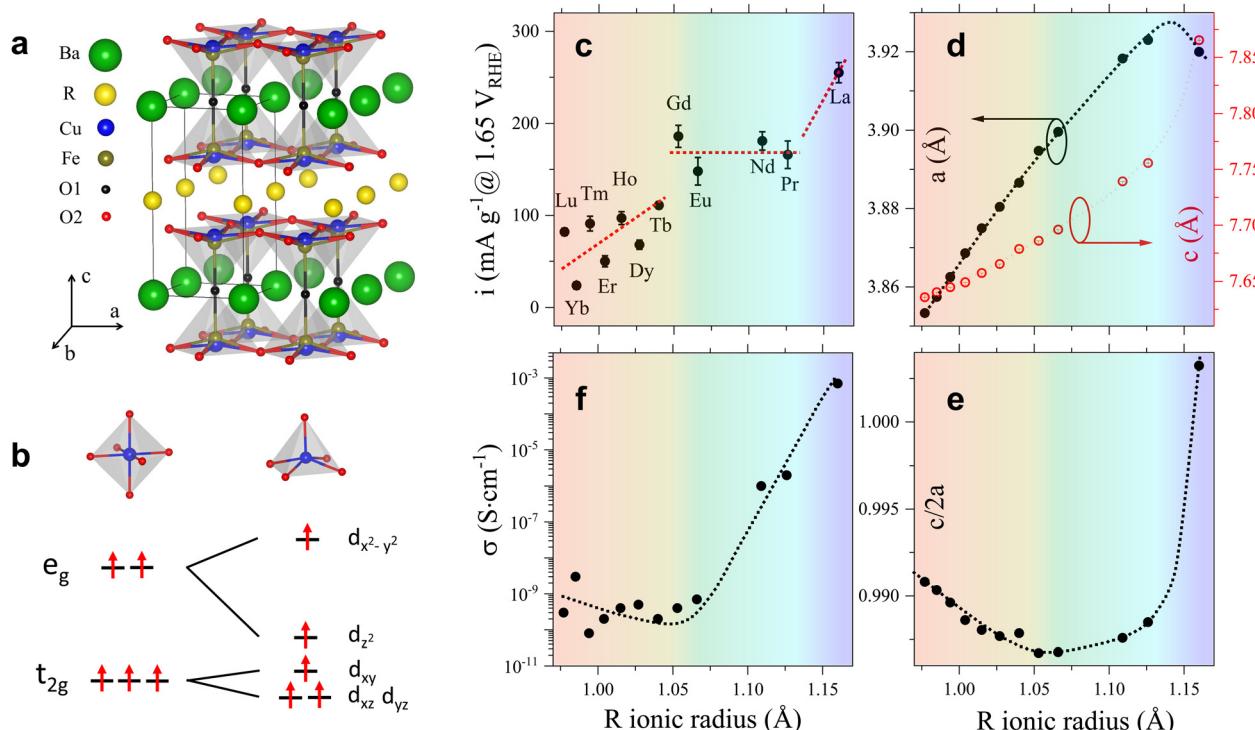
Here, we use this knob to tune the electrocatalytical performance in the  $\text{RBaCuFeO}_{5+\delta}$  family. Our measurements reveal a complex modification of the OER activity upon 4f cation replacement, which shows no direct correlation with the lanthanide ionic radius ( $R_{\text{ionic}}$ ) or the electric conductivity  $\sigma$ . We rationalize these results in terms of the changes in the crystal and electronic structures that we investigate here in detail using a combination of *ab initio* calculations and advanced neutron and X-ray synchrotron techniques. The results of this combined analysis uncover an intriguing dependence of the OER activity on the parity of the 4f electron count for the compounds with  $\delta = 0$ . Moreover, they reveal a positive impact of the oxygen excess ( $\delta > 0$ ) in the conductivity, which leads to the partial oxidation of  $\text{Fe}^{3+}$  into  $\text{Fe}^{4+}$  while keeping the  $\text{Cu}^{2+}$  valence nearly constant. This results in a sharp rise of the Fe–O hybridization and in the creation of new hole-states in the gap, whose combined effect is at the origin of the abrupt increase of  $\sigma$  upon oxygen uptake. Contrarily to the results reported for some 3D Fe-based perovskites,<sup>25</sup> growing values of  $\text{Fe}^{4+}$  (and  $\sigma$ ) alone do not grant a simultaneous increase of the OER activity, which requires also sufficient weakly bound oxygen and a distribution of oxygen vacancies that ensures enough two-dimensional oxygen diffusion channels in the catalysts'bulk. This observation suggests an active participation of the perovskite lattice oxygen in the OER process, the lattice oxygen evolution reaction (LOER), theoretically postulated<sup>26,27</sup> and experimentally supported<sup>28–30</sup> by some previous studies. To conclude, we show that the material with the best figures of merit of this study ( $\text{LaBaCuFeO}_{5.49}$ ) can reach intrinsic OER activities approaching those of Co-based oxide perovskites and can be industrially produced in nanocrystalline form.

## 2. Results

### 2.1. OER activity of $\text{RBaCuFeO}_{5+\delta}$ layered perovskites

The crystal structure of the  $\text{RBaCuFeO}_{5+\delta}$  layered perovskites with  $\delta = 0$ , shown in Fig. 1a, is characterized by a tetragonal unit cell  $a_c \times a_c \times c$  ( $c \approx 2a_c$ ) where  $a_c$  denotes the pseudocubic perovskite unit-cell parameter.<sup>24</sup> The doubling of the  $c$ -parameter is due to the ordering of the A-cations  $\text{R}^{3+}$  and  $\text{Ba}^{2+}$  in layers perpendicular to this crystal axis, which is triggered by the large difference in ionic radius between the lanthanides and barium. The B positions are occupied by  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ , which contrarily to the A-cations, display some preparation-dependent degree of disorder.<sup>31,32</sup> This chemical disorder is represented in Fig. 1a by the splitting of the B site inside the pyramids, where Cu and Fe have slightly different  $z$ -coordinates. An important difference with 3D perovskites is





**Fig. 1** (a) Crystal structure of the RBaCuFeO<sub>5+δ</sub> compounds with  $\delta = 0$ . The figure highlights the R/Ba order in the A-sites, the Cu/Fe disorder in the B-sites, and the absence of oxygen in the R-layers. (b) Splitting of the transition metal 3d orbitals under the action of octahedral and square-pyramidal crystal fields. (c)–(f) Modification of the OER activity, lattice parameters ( $a$  and  $c$ ),  $c/2a$  ratio and electric conductivity  $σ$  upon R-cation replacement. The error bars in (c) and (f) are the standard deviations obtained after repeating the measurements at least three times. In (d) they are the values provided by the Rietveld software FullProf Suite, and in (e) they have been calculated from the (d) values using error propagation formulas. The color background highlights the regions with different dependence of the OER activity with  $R_{\text{ionic}}$ . Dotted lines are guides for the eye.

that the B-cations are in square-pyramidal coordination due to the existence of 1/6 of ordered oxygen vacancies localized in the lanthanide layers. This leads to the stabilization of the  $d_{xz}$ ,  $d_{yz}$  and  $d_{z^2}$  orbitals with respect to the energies of the  $t_{2g}$  and  $e_g$  levels of octahedral parentage, as shown schematically in Fig. 1b. The stabilization is particularly pronounced in the case of  $d_{z^2}$ , which as we show later, may reach energies close to that of the  $t_{2g}$  orbitals. It is worth mentioning that the lanthanide layers can incorporate additional oxygen ( $1 > \delta > 0$ ), which for intermediate compositions, leads to the coexistence of B-cations in square-pyramidal and octahedral coordination.<sup>33–35</sup>

Since the focus of this investigation was on identifying the critical variables leading to the best OER catalytic performance, we compared first the changes in the OER activity upon R cation replacement with those observed in several structural variables, namely, lattice parameters, interatomic distances and angles, oxygen content, oxygen vacancy distribution and degree of cation intermixing. A necessary condition to obtain precise values of these quantities is the use of well-crystallized materials. We thus synthesized twelve RBaCuFeO<sub>5+δ</sub> ceramic samples with R = La, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu using the solid-state reaction technique, which yields powders with large particle sizes and narrow Bragg reflections in the powder diffraction patterns (ESI†). Another crucial point is the use of analytical techniques able to determine precisely the

atomic coordinates of the different O sites, their occupations and their anisotropic mean-square displacements (MSD). We thus employed powder neutron diffraction (PND), more sensitive than X-ray diffraction to light elements such as oxygen. The obtained structural data were used as starting point for density functional theory (DFT) calculations, employed here to interpret the X-ray absorption spectroscopy (XAS) measurements, and to investigate the evolution of different electronic variables (band gap, energy position of the empty states associated to the different 3d orbitals, centre of gravity of the O valence band, TM–O covalency, and electron filling of the Cu and Fe 3d orbitals), proposed in the recent literature as OER descriptors.<sup>3</sup> The changes in the OER activity upon replacement of the 4f R-cation were then contrasted with those observed in the different structural and electronic parameters in order to uncover their degree of correlation with the OER electrochemical performance.

The OER activity of all samples was measured in a three-electrode cell configuration as described in the ESI.† The measured currents in the OER region were initially stabilized with a series of cyclic voltammetry measurements between 1 and 1.7 V<sub>RHE</sub>, during which the activity of most of the RBaCuFeO<sub>5+δ</sub> electrocatalysts increased over cycling (Fig. S1a, ESI†). The largest activity increment was obtained in the initial 14 cycles with an average increase of ~70% of the current

recorded in the 2nd cycle. The Tafel slopes, the mass-specific current density at 1.65 V<sub>RHE</sub> and the overpotentials at 10 mA g<sup>-1</sup> of the RBaCuFeO<sub>5+δ</sub> samples are listed in Table S1 (ESI†), while the Tafel plots are shown in Fig. S2 (ESI†).

The OER electrochemical activities of the twelve RBaCuFeO<sub>5+δ</sub> samples, expressed as gravimetric current densities at 1.65 V<sub>RHE</sub>, are shown in Fig. 1c as a function of the R ionic radius. Due to the large particle size of our samples, their surface areas were too small to be accurately determined by Brunauer–Emmett–Teller (BET)<sup>36</sup> measurements. This prevented the evaluation of surface area normalized current densities. However, from the comparable size and shape of the particles, as estimated from scanning electron microscopy (SEM) and from X-ray powder diffraction using the Scherrer formula, and the akin double layer capacitances (Fig. S1b, ESI†), similar behaviors of the gravimetric and surface-normalized activities along the 4f series can be reasonably expected (Materials and methods, Fig. S3 and Table S2, ESI†). As shown in Fig. 1c, the OER electrocatalytic activity is the highest for R = La, the lanthanide with the largest atomic radius. Although smaller R ionic radii result in general on a lower electrocatalytic performance, the OER activity is not a linear function of  $R_{\text{ionic}}$ , with deviations from linearity well beyond the error bars. Instead, three different regimes are clearly observed. In the first one, the activity alternates with the occupation of the 4f orbitals, with higher values for cations with even 4f occupations (Lu<sup>3+</sup>, Tm<sup>3+</sup>, Ho<sup>3+</sup>, Tb<sup>3+</sup>) and lower for those with odd occupations (Yb<sup>3+</sup>, Er<sup>3+</sup>, Dy<sup>3+</sup>). In the second (Gd<sup>3+</sup>, Eu<sup>3+</sup>, Nd<sup>3+</sup>, Pr<sup>3+</sup>), the activity is approximately constant. In the third (La<sup>3+</sup>), a substantial activity jump with respect to the previous region is observed. These results are at odds with the behaviour expected from the monotonic increase of the R ionic radius along the 4f series, and suggest that additional variables may be controlling the OER activity. As we show in the next sections, several structural and electronic descriptors show anomalies at the same  $R_{\text{ionic}}$  values that define the three OER activity regions.

## 2.2. Modification of the crystal structure upon insertion of increasingly larger lanthanides

**Lattice parameters.** To get insight into the mechanism behind the evolution of the electrochemical response we investigated the modifications of the layered perovskite framework induced by the insertion of the different lanthanides. High-resolution structural data have been reported previously by some of us for the smallest 4f cations (Lu to Dy) using PND,<sup>18</sup> and we complete them here for R = Tb, Gd, Eu, Nd, Pr and La. For the compounds with R = Eu and Gd, where the high neutron absorption cross-section of these cations prevents the use of PND, we used powder X-ray diffraction (PXRD) instead (Fig. S4, S5 and Tables S2, S3, ESI†).

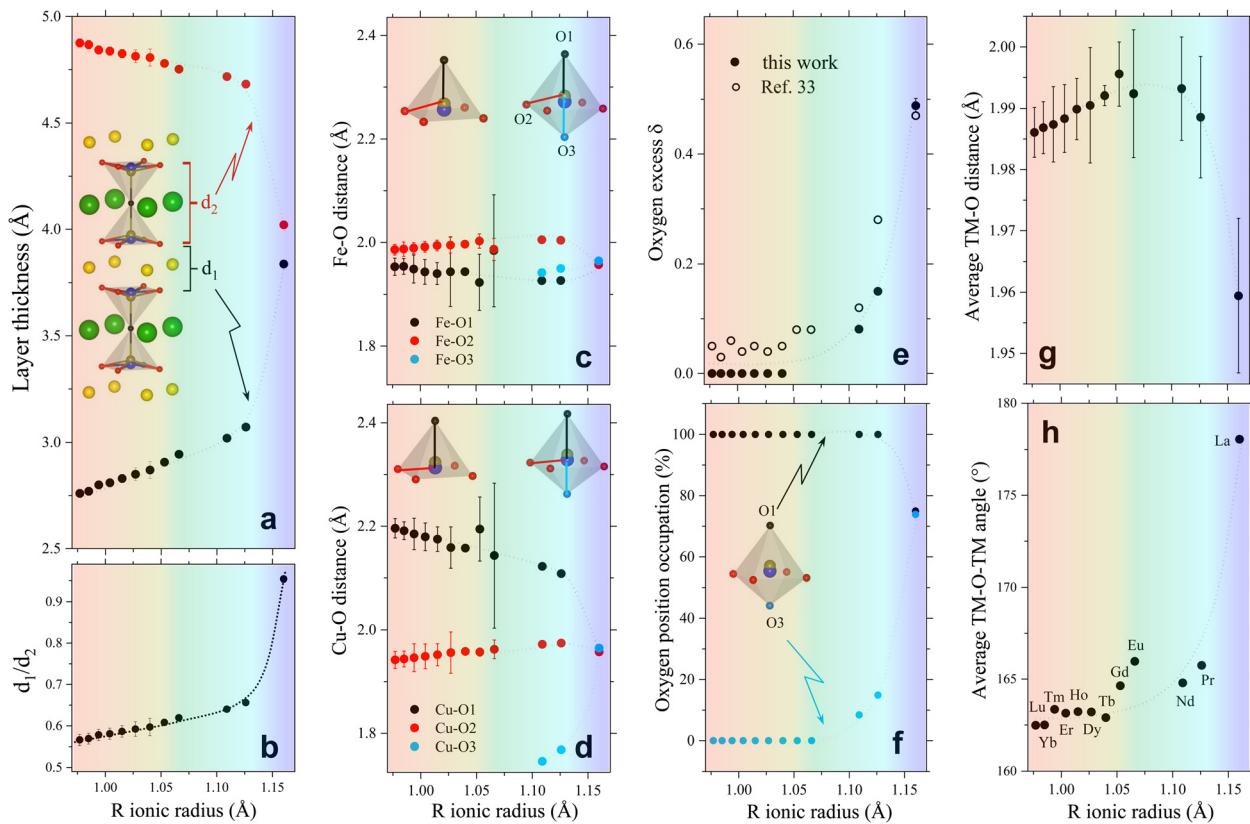
Fig. 1d and Table S2 (ESI†) show the modification of the lattice parameters  $a$  and  $c$  with the R-cation ionic radius. As expected, both increase with  $R_{\text{ionic}}$ . However, their evolution along the 4f series differs from the linear increase expected from Vegard's law and observed in other structurally-related

perovskites.<sup>37</sup> This deviation is better appreciated in Fig. 1e, showing the changes in the tetragonal distortion  $c/2a$  of the pseudocubic unit cell with  $R_{\text{ionic}}$ , where  $c/2a = 1$  corresponds to a RBaCuFeO<sub>5+δ</sub> layered perovskite containing two perfectly cubic perovskite units. For the smaller lanthanides (Lu to Gd)  $c/2a$  takes values smaller than one and decreases with  $R_{\text{ionic}}$ , indicating a tensile distortion that becomes more pronounced for growing R ionic radii. For R = Gd, exactly in the middle of the 4f series, this tendency is reversed, and  $c/2a$  increases with  $R_{\text{ionic}}$  until R = Pr. For LaBaCuFeO<sub>5+δ</sub>, the last member of the series,  $c/2a$  undergoes a huge increase, rising up to a value slightly larger than 1. The tetragonal distortion of this material is thus slightly compressive, and much smaller than in the rest of the family. Interestingly, the variation of  $c/2a$  defines three distinct regions that nicely coincide with those inferred from that of the OER activity. We also note that the  $c/2a$  minimum is very close to that observed in the electric conductivity  $\sigma$  (Fig. 1f) that, as the OER activity, does not change in a monotonic way with the R ionic radius.

**Interatomic distances, angles, oxygen content, oxygen vacancy distribution and A-cation intermixing.** To rationalize these observations we examined the evolution of several interatomic distances and angles along the series, and compared them with the behaviour of the electrochemical response. Fig. 2a shows the changes in the separation between the bipyramidal slabs  $d_1$  (directly related to the lanthanide size) and the slab thickness  $d_2$ . As expected,  $d_1$  increases linearly with  $R_{\text{ionic}}$ .  $d_2$ , in contrast decreases, albeit to a slightly slower rate. Interestingly, both trends are sharply interrupted for R = La, where the large difference between  $d_1$  and  $d_2$  observed in the remaining RBaCuFeO<sub>5+δ</sub> compounds ( $d_2 = \sim 1.7d_1$ ) disappears and both distances become nearly identical (Fig. 2b). This suggests the existence of an important structural reorganization in LaBaCuFeO<sub>5+δ</sub> that, as shown in Fig. 1f and c, results in a substantial increase in both, the conductivity (note the log scale) and the OER activity.

To verify this point, we had a closer look at the changes within the bipyramidal slabs, which host the B-cations Fe and Cu. Fig. 2c and d show the evolution of the in-plane and out-of-plane distances in the FeO<sub>5</sub> and CuO<sub>5</sub> pyramids. We note that the Fe coordination polyhedron is extremely regular, as expected from its symmetric Fe<sup>3+</sup> high-spin electronic configuration ( $t_{2g}^3 e_g^2$ ), with one electron per 3d orbital. In contrast, the CuO<sub>5</sub> pyramids are strongly distorted, with four short in-plane distances and a very long apical distance, in line with the Cu<sup>2+</sup> Jahn–Teller active configuration ( $t_{2g}^6 e_g^3$ ). As shown in Fig. 2c and d, the distortion of the Fe and Cu coordination polyhedra changes very little with the lanthanide size for the compounds with R = Lu to Eu. In contrast, a major modification is observed for those with R = Nd, Pr and La, where the Rietveld fits of the PND data indicate the presence of additional oxygen (O3) in the R-layers (Fig. 2e and f). The correct stoichiometry for these compounds is thus RBaCuFeO<sub>5+δ</sub>, with  $\delta = 0.081(1)$ ,  $0.150(5)$  and  $0.49(1)$  for Nd, Pr and La, respectively. This contrasts with the compounds with the smallest lanthanides (Lu to Tb), where  $\delta = 0$  within the PND detection limit. For R = Gd and Eu the





**Fig. 2** Evolution of different crystallographic descriptors with the R-cation ionic radius in  $\text{RBaCuFeO}_{5+\delta}$  layered perovskites. (a) Thickness of the R-containing layers ( $d_1$ ) and the bipyramidal layers ( $d_2$ ). (b)  $d_1/d_2$  ratio. (c) Fe–O interatomic distances. (d) Cu–O interatomic distances. (e) Oxygen excess  $\delta$ . (f) Occupation (in %) of the two apical position O1 and O3. (g) Average TM–O distance. (h) Average TM–O–TM superexchange angle. The atomic positions and occupations employed to calculate these descriptors are from our previous work (Lu to Dy),<sup>18</sup> and from this study (Tb to La, Table S3, ESI†). They were all determined from high-resolution PND data with the exception of R = Gd and Eu (ESI†). Dotted lines are guides for the eye. The color background highlights the regions with different dependence of the OER activity with  $R_{\text{ionic}}$ .

impossibility to perform PND measurements prevents the determination of the oxygen content and its distribution in the structure. However, a quadratic extrapolation suggests that the oxygen uptake could already start for R = Gd. Interestingly, it is precisely for R = Gd where a discontinuity in the evolution of the tetragonal distortion  $c/2a$  (Fig. 1e), the OER activity (Fig. 1c) and the electric conductivity (Fig. 1f) is observed.

Besides revealing the incorporation of additional oxygen in the R-layers for the larger lanthanides, the changes observed in the Fe–O and Cu–O interatomic distances confirm the anomalous behaviour of  $\text{LaBaCuFeO}_{5.49}$ . At odds with the rest of the series, the basal and apical distances of this compound are nearly identical for the Cu and Fe coordination polyhedra (Fig. 2c and d). Moreover, PND reveals not only a large O excess ( $\delta = 0.49$ ) but also the existence of a significant number of vacancies in the apical oxygen position O1, fully occupied in the remaining members of the family (Fig. 2f). For R = La, the distribution of the extra O and the O-vacancies in the structure is thus completely different from that observed in the other compounds. The reason behind is the intermixing of the  $\text{La}^{3+}$  and  $\text{Ba}^{2+}$  cations, which results in a dramatic structural homogenization of the two pseudocubic units in the layered perovskite structure (Table S3, ESI†). Ba (green) and the R cations

(yellow) are indeed perfectly ordered for R = Lu to Pr (Fig. 1a). However, this is not anymore the case for R = La, where about 55% of the  $\text{Ba}^{2+}$  sites are occupied by  $\text{La}^{3+}$  cations (and *vice versa*) due to the similarity between their ionic radii. This breaks the perfect alternation of the A-site cations along the crystallographic *c*-direction observed for the other lanthanides, allowing the creation of O vacancies also in the Ba layers thanks to the simultaneous presence of  $\text{La}^{3+}$ , which prefers lower O-coordination than  $\text{Ba}^{2+}$ . The resulting decrease of layered character leads to a pseudo-cubic unit cell with  $c/2a$  ratio very close to 1 (Fig. 1e). We note that a small tetragonal distortion ( $c/2a = 1.0032$ ) is nevertheless preserved due to the combined impact of the slightly asymmetric  $\text{La}^{3+}/\text{Ba}^{2+}$  distribution in the two A-sites, and a small difference in the percentage of oxygen vacancies at the O1 and O3 apical sites ( $\approx 25(1)\%$  and  $\approx 26.1(1)\%$ , respectively, Fig. 2f). As we will see in the next sections, this residual distortion has an important impact on the oxygen displacement pattern in the structure.

**Link between crystal structure and electric conductivity.** Since the electric conductivity  $\sigma$  is linked to the bandwidth, which depends on the degree of Cu/Fe 3d–O 2p overlap  $W$ , we can use our structural data to estimate this quantity and to check whether it scales with  $\sigma$ . We employ here the expression

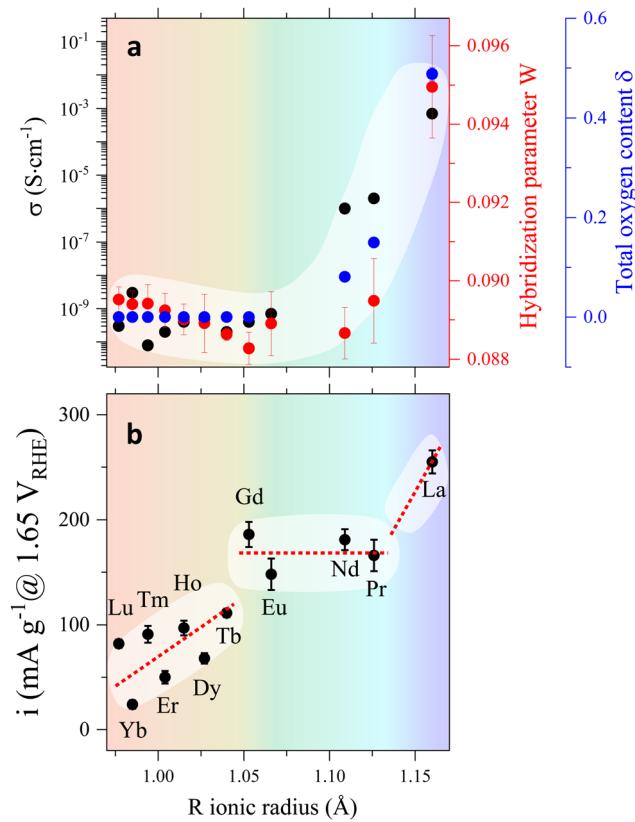


Fig. 3 (a) Evolution of the electric conductivity  $\sigma$ , the hybridization parameter  $W = \cos[(180 - \theta)/2]/d_{\text{TM}-\text{O}}^{3.5}$  and the oxygen excess  $\delta$  with the R ionic radius. The plot highlights the correlation between  $\sigma$ ,  $\delta$  and  $W$ , and the lack of correlation between the evolution of these three variables and that of the OER activity, shown in (b).

$W = \cos[(180 - \theta)/2]/d_{\text{TM}-\text{O}}^{3.5}$  reported in ref. 38 and 39 which reflects the positive impact of short average TM–O distances  $d_{\text{TM}-\text{O}}$  and large average TM–O–TM superexchange angles  $\theta$  in the degree of TM–O overlap. The  $W$  values obtained using the experimental values of  $d_{\text{TM}-\text{O}}$  (Fig. 2g) and  $\theta$  (Fig. 2h) are shown as red markers in Fig. 3a, together with those of  $\sigma$  (black) and  $\delta$  (blue). We observe strong similarities between the behaviour of  $W$  and  $\sigma$  along the series, namely, low values and a smooth decrease with  $R_{\text{ionic}}$  for the compounds with  $\delta = 0$ , a minimum around  $R = \text{Gd}$ , and an abrupt increase as soon as additional oxygen (O3) is incorporated in the R layers. This last observation suggests that the partial occupation of the O3 position breaks the physical isolation of the CuO<sub>5</sub>–FeO<sub>5</sub> bipyramidal slabs along the  $c$  axis thanks to the creation of new TM–O bonds, which open a new electronic conduction channel in the structure and increase the degree of TM–O overlap (Fig. 3a). Surprisingly, this conductivity increase has little effect on the OER activities of the compounds with  $R = \text{Gd}$ , Eu, Nd and Pr, which remain nearly constant (Fig. 3b). In contrast, a clear, discontinuous increase is observed for  $R = \text{La}$  coinciding with the appearance of La/Ba intermixing and the creation of oxygen vacancies in the O1 apical positions.

**Anisotropic mean-squared displacements, O mobility and link to OER activity.** A key to understand these unexpected

observations is given by the dramatic change in the shape of the anisotropic thermal ellipsoids in LaBaCuFeO<sub>5.49</sub>, particularly those of the oxygen sites. As shown in Fig. S6 (ESI†) and Fig. 4a and b, PND reveals anisotropic thermal ellipsoids relatively small and slightly elongated along the  $c$  direction for  $R = \text{Lu}$  to Pr. In contrast, a huge change in size and shape is observed for  $R = \text{La}$ , where the largest ellipsoid axes correspond now to atomic displacements in the  $ab$  plane (Fig. 4c). The observation of larger in-plane atomic displacement parameters may arise from the quasi-random static ionic displacements associated to the Ba/La intermixing, the increase on the O3 occupation, and the appearance of vacancies in the O1 position. However, they can also be due to the onset of the oxygen diffusion in the  $ab$  planes.<sup>40</sup> Based on the crystallographic data alone it is not possible to distinguish between these two possibilities. However, the simultaneous observation of a large increase in both, the electric conductivity and the OER activity suggests that the second possibility is not unlikely. It is well established that the mobility of diffusing ions in ionic conductors largely depends on the connectivity between the available hopping sites. The existence of oxygen vacancies in the two apical positions is thus expected to favor in-plane O1 and O3 hopping (Fig. 4d–f), and is consistent with the disk-shape of their thermal ellipsoids. For the O2 position, our PND data could not reveal the presence of oxygen vacancies. Hence, their large mean-squared displacements in the  $ab$  plane are most probably a static response to the O and R/Ba chemical disorder.

To summarize, our results indicate that the behaviour of the electric conductivity in RBaCuFeO<sub>5+δ</sub> layered perovskites is closely linked to the modification of the crystal structure upon R cation replacement, and in particular, to its impact on the Cu/Fe 3d – O 2p overlap  $W$ . This parameter, which depends on the average values of the TM–O distances and TM–O–TM angles, was calculated exactly from the PND structural data, and its evolution with  $R_{\text{ionic}}$  was found to scale with that of  $\sigma$ . However, neither  $W$  nor  $\sigma$  scale with the OER activity, which also depends on the details of the A-cation and O vacancy distribution in the layered structure. Hence, improving conductivity though the incorporation of additional O does not grant an increase in the OER activity in RBaCuFeO<sub>5+δ</sub> layered perovskites, which also requires a distribution of oxygen vacancies in the structure that provides sufficient weakly bonded oxygen and enough oxygen diffusion pathways. This last scenario, realized in LaBaCuFeO<sub>5.49</sub>, suggests the involvement of the lattice oxygen in the OER process for this material, where the reaction mechanism could be the theoretically postulated LOER.<sup>26–30</sup>

### 2.3. Stability of the Cu and Fe oxidation states

The impact of the initial B-cation electronic configuration in the OER activity has been intensively debated in the literature, particularly for Co-based perovskites, and there is increasing evidence suggesting that it plays an essential role in the catalyst electrochemical behaviour and OER performance.<sup>1,2</sup> In RBaCuFeO<sub>5+δ</sub> perovskites the best figures of merit are found for the O-rich samples, but the B-position is occupied by two different



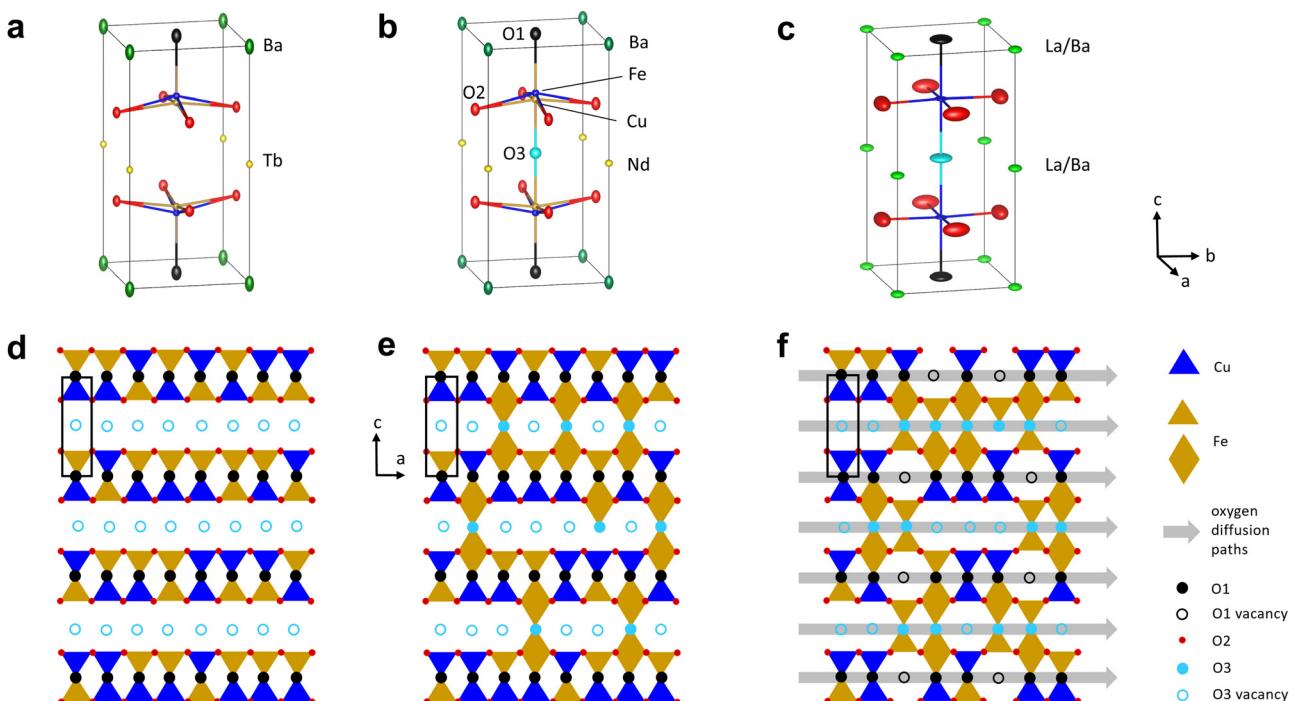


Fig. 4 (a)–(c) Thermal ellipsoids (60% probability) at RT for TbBaCuFeO<sub>5.00</sub> (R/Ba order,  $\delta = 0$ ), NdBaCuFeO<sub>5.08</sub> (R/Ba order,  $\delta > 0$ ) and LaBaCuFeO<sub>5.49</sub> (R/Ba intermixing,  $\delta > 0$ , apical O sites O1 and O3 partially occupied). (d)–(f) Schematic representation of the O vacancy distribution and the O diffusion paths suggested by the combined structural (PND) and spectroscopic (XAS) analysis, which represent the three different situations shown in (a)–(c). The Ba<sup>2+</sup> and R<sup>3+</sup> cations are not shown for clarity.

cations. A pertinent question is thus which one among them (Cu<sup>2+</sup> or Fe<sup>3+</sup>) will be the most prone to provide electrons that compensate the incorporation of additional oxygen in the structure, and what will be the resulting 3d orbital occupation(s). A technique that can provide insight on the changes in the Cu and Fe electronic configuration is X-ray absorption spectroscopy (XAS), which can selectively probe the empty states of the different atomic species (ESI†).

**4f lanthanide M-edges.** In oxide perovskites, R cations are usually assumed to be inert, formally trivalent spacers with electronic configurations 4f<sup>n</sup>, with  $n$  taking values between 0 (La) and 14 (Lu). However, some lanthanides (among them Ce, Pr and Tb) may display both, +3 and +4 oxidation states depending on the synthesis conditions. Since the stabilization of tetravalent R cations may have an impact in the valence assignation of Fe and Cu, we investigated the R oxidation state in the full series by examining the M edges of the R cations, which probe the unoccupied density of R 4f states. The main contribution to these edges comes from the excitation of electrons from the spin-orbit-split levels 3d<sub>5/2</sub> and 3d<sub>3/2</sub> into empty states of 4f symmetry, which appear as two intense, well-separated line groups denoted as M<sub>5</sub> and M<sub>4</sub>, respectively. The M<sub>5,4</sub> lines are characterized by a fine structure that is governed by the Coulomb and exchange interaction between the 3d<sup>9</sup> core hole and the 4f electrons. Since these interactions depend on the number of electrons in the 4f shell, the details of the fine structure are characteristic of each 4f electronic configuration. Transitions from 3d levels into empty 6p states are also

dipole-allowed, but their intensity is much weaker than that of the M<sub>5,4</sub> lines, in particular for the lanthanides with a large number of 4f holes.

The M edges measured for our twelve RBaCuFeO<sub>5+δ</sub> samples using the total electron yield (TEY) mode are shown Fig. S7 (ESI†). For R = Lu, the absence of the M<sub>5,4</sub> lines brings to light the weak 3d → 6p signal, indicating a full 4f<sup>14</sup> occupation consistent with the presence of Lu<sup>3+</sup>. The M<sub>5,4</sub> lines are well visible in the remaining spectra, and we have compared their fine structures with those reported in ref. 41 for well characterized oxides with trivalent R cations, as well as with the calculations of Thole *et al.*<sup>42</sup> A detailed comparison was not possible for R = Pr due to the superposition between the Pr M<sub>5,4</sub> and the Cu L<sub>3,2</sub> edges. However, for remaining R-cations, the comparison shows that all our M<sub>5,4</sub> spectra correspond to 4f lanthanides in a triply ionized ground state. Given that they were recorded in TEY mode, which probes mainly the surface of the catalyst's particles (2–5 nm), we can conclude that the nominal bulk valence of R cations in our RBaCuFeO<sub>5+δ</sub> layered perovskites (+3) is preserved in the particle's surface, where they remain trivalent for all the compounds investigated.

**Fe and Cu K-edges.** The high penetration of the energies associated to the Fe and Cu K-edges (~7 and ~9 keV respectively) make them ideal probes to investigate the oxidation state of these elements in the particle's bulk. Fig. S8a (ESI†) shows the Fe K-edge X-ray absorption near-edge spectra region measured for the compounds with R = Lu, Yb, Tm, Er, Ho, Dy, Tb and La. This edge cannot be accessed for the remaining

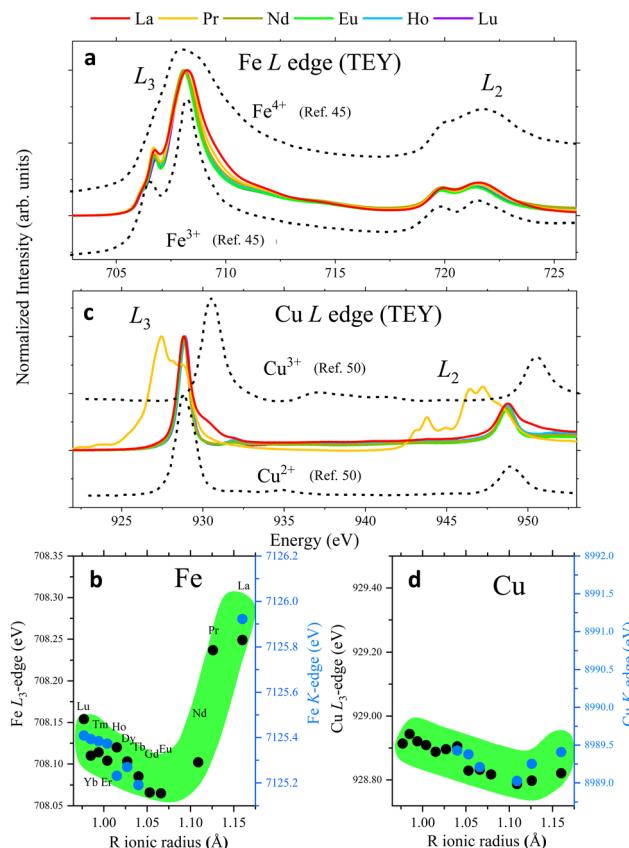


Fig. 5 L and K-edge features of representative  $\text{RBaCuFeO}_{5+\delta}$  layered perovskites (see also Fig. S8 and S9, ESI†). (a) Fe L-edges. (b) Left axis: maximum of the Fe K-edges's 1st derivative; right axis: Fe  $L_3$ -edges's maximum. (c) Cu L-edges. The different shape for  $\text{R} = \text{Pr}$  is due to the superposition with the Pr  $M_{5,4}$  edges (see also Fig. S7, ESI†). (d) Left axis: maximum of the Cu K-edges's 1st derivative; right axis: Cu  $L_3$ -edges's maximum. All L-edges were measured using the TEY mode.

compounds ( $\text{R} = \text{Gd}$  to  $\text{Pr}$ ) due to the overlap with the L-edges of the R cations. However, this reduced set includes representatives of the  $\delta = 0$  (Lu to Tb) and  $\delta > 0$  (La) stoichiometries. The main contribution to the 3d TM K-edges comes from the excitation of TM 1s core electrons into empty states of 4p symmetry. The information about the TM 3d filling is thus only indirect. However, for absorbers with the same ligands and the similar coordination polyhedra, the energy position of the main absorption threshold, which we define here as the maximum of the edge's first derivative (Fig. S8b, ESI†), has been shown to correlate positively with the cation oxidation state.<sup>43</sup> For the compounds with  $\text{R} = \text{Lu}$  to  $\text{Tb}$ , the edge position (Fig. S8c (ESI†) and blue markers in Fig. 5b) displays little changes with the R ionic radius, the only appreciable modification being a smooth displacement of the edge position towards lower energies ( $\Delta E \sim -0.22$  eV). Given the perfect oxygen stoichiometry of these compounds, this is probably linked to the small increase of the average Fe–O distance with  $R_{\text{ionic}}$ , which according to Natoli's rule<sup>44</sup> should result in a small energy displacement proportional to the inverse of the squared average bond length. This smooth evolution is abruptly

reversed for  $\text{LaBaCuFeO}_{5.49}$ , the compound with the highest OER activity, whose Fe K-edge undergoes a huge displacement towards higher energies ( $\Delta E \approx +0.73$  eV) when moving from  $\text{R} = \text{Tb}$  to La. This observation strongly suggests that the extra oxygen incorporated by this material results in a substantial increase of the Fe oxidation state, possibly because of a preferential bonding to this transition metal.

If the extra oxygen binds preferentially to the Fe sites, most of the (nominally divalent) Cu sites will preserve the square-pyramidal coordination, and the Cu oxidation state will remain nearly unchanged (Fig. 4f). To check whether this is the case we examined the evolution of the Cu K-edges. Due to overlap with the L-edges of the R-cations, the only accessible Cu K-edges are those of the compounds with  $\text{R} = \text{Tb}$ ,  $\text{Gd}$ ,  $\text{Eu}$ ,  $\text{Nd}$ ,  $\text{Pr}$  and  $\text{La}$  (Fig. S8d, ESI†). Luckily, this reduced set also includes representatives of the  $\delta = 0$  (Tb) and  $\delta > 0$  stoichiometries (Gd to La). As shown in Fig. 5d (blue markers) and Fig. S8f (ESI†), the edge position decreases smoothly with  $R_{\text{ionic}}$  for  $\text{R} = \text{Tb}$ ,  $\text{Gd}$ ,  $\text{Eu}$  and  $\text{Nd}$ , where  $\delta$  is either 0 or very small. Since the average Cu–O distance also increases with  $R_{\text{ionic}}$ , this is most probably another manifestation of the Natoli's rule. For  $\text{R} = \text{Pr}$  and  $\text{La}$ , with  $\delta$  values substantially larger, this tendency is broken, and the edge positions move to slightly higher energies. The displacement is however much smaller than in the case of the Fe K-edges. To illustrate this point we can compare the positions of the Tb and La samples in the Fe and Cu K-edges. The Fe K-edge of the La sample is +0.73 eV higher than the one with Tb. In contrast, the Cu K-edge positions of both samples are nearly identical. This suggests that the electrons needed to compensate the incorporation of oxygen in the structure are primarily provided by  $\text{Fe}^{3+}$ , which partially oxidizes to  $\text{Fe}^{4+}$ . The  $\text{Cu}^{2+}$  valence appears to be more robust against oxidation, but for  $\text{R} = \text{Pr}$  and  $\text{La}$  our data suggest that  $\text{Cu}^{2+}$  oxidizes partially to  $\text{Cu}^{3+}$ , albeit in a much smaller amounts. It is worth mentioning that these conclusions apply to the sample bulk. However, we will show in the next section that the analysis of the Fe and Cu L-edges measured using the TEY mode supports a similar behaviour also in the particle's surface.

**Fe and Cu L-edges.** The main contribution to the Fe and Cu L-edges comes from the excitation of electrons from the spin-orbit-split levels  $2p_{3/2}$  and  $2p_{1/2}$  into empty states of 3d symmetry. This results in two strong absorption lines, ( $L_3$  and  $L_2$  edges, respectively) whose shape and fine structure encode information about the absorber's electronic configuration. The Fe L-edges of the twelve  $\text{RBaCuFeO}_{5+\delta}$  layered perovskites measured using the TEY mode are displayed in Fig. 5a and Fig. S9a (ESI†). For the samples with  $\delta = 0$  ( $\text{R} = \text{Lu}$  to  $\text{Eu}$ ) the spectra are very similar to the Fe L-edge of  $\text{LaFeO}_3$  reported in ref. 25 and 45 where Fe is nominally trivalent. However, their shape starts to change as soon as O is incorporated in the structure. The changes are particularly pronounced for the  $L_3$  edges, where the sharp feature at  $\sim 707$  eV smears out, additional intensity appears at energies between 709–711 eV, and the  $L_3$  maximum moves towards higher energies. Since the L-edges of  $\text{SrFeO}_3$ <sup>25,45</sup> and  $\text{BaFeO}_3$ ,<sup>46</sup> where Fe is nominally tetravalent, share these characteristics, the evolution of the L-edges in the O-rich samples ( $\text{R} = \text{Nd}$ ,  $\text{Pr}$  and  $\text{La}$ ) strongly



suggests a progressive oxidation of  $\text{Fe}^{3+}$  to  $\text{Fe}^{4+}$  upon O uptake (see also Fig. S9a, ESI<sup>†</sup>). The strong broadening of the  $\text{SrFeO}_3$  L-edge, more pronounced than that of  $\text{LaBaCuFeO}_{5.49}$  (the material with the highest O content of this study) suggests nevertheless that the  $\text{Fe}^{3+} \rightarrow \text{Fe}^{4+}$  oxidation is incomplete for all the samples investigated.

The different behaviour of the O-poor ( $\delta = 0$ ) and O-rich samples is illustrated in Fig. 5b, where the black symbols show the evolution of the  $\text{L}_3$  maximum with  $R_{\text{ionic}}$ . For  $R = \text{Lu}$  to  $\text{Eu}$  we observe a small displacement towards lower energies, possibly related with the small changes in the square-pyramidal crystal field splitting with  $R_{\text{ionic}}$  (Fig. 2c).<sup>47</sup> In contrast, the  $\text{L}_3$  maximum undergoes a sharp displacement towards higher energies for  $R = \text{Nd}$ ,  $\text{Pr}$  and  $\text{La}$ , where oxygen is progressively incorporated to the structure. Given that the spectra were measured using the TEY detection mode, these changes are expected to reflect the Fe oxidation in the particle's surface. Interestingly, a comparison between the evolution of the  $\text{L}_3$  maximum and the position of the Fe K-edge along the series (black and blue markers in Fig. 5b, respectively) reveals a nice scaling between the two sets of data, and suggests that Fe oxidizes upon O incorporation both, in the bulk and in the surface.

We compare now this behaviour with that of the Cu L-edges. As shown in Fig. 5c and Fig. S9b (ESI<sup>†</sup>), the spectra of the materials with  $R = \text{Lu}$  to  $\text{Nd}$  are very similar to that reported for  $\text{CuO}$ <sup>48,49</sup> or some Cu(n) complexes<sup>50</sup> where Cu is nominally divalent. For  $R = \text{Pr}$  some changes start to become evident, but they are partially hidden by the overlap with the Pr  $\text{M}_{5,4}$  lines (Fig. S7, ESI<sup>†</sup>). This tendency is confirmed for  $R = \text{La}$ , where new features (see also Fig. S9b, ESI<sup>†</sup>) are clearly observed at energies very close to those of the  $\text{L}_3$  and  $\text{L}_2$  lines of  $\text{NaCuO}_2$ ,<sup>48,49</sup> where Cu is nominally trivalent.

As in the case of the Fe L-edges, the Cu  $\text{L}_3$  maximum moves slightly towards lower energies by increasing the R ionic radii (black markers in Fig. 5d), an observation that we also ascribe to changes in the crystal field splitting of the  $\text{CuO}_5$  pyramids (Fig. 2d). This tendency changes for  $R = \text{Pr}$  and  $\text{La}$ , where the energy position of the  $\text{L}_3$  maximum moves slightly towards higher energies. However, the displacement is much less pronounced than in the case of the Fe  $\text{L}_3$  edge. This behaviour is again very similar to that of the Cu K-edges (blue markers in Fig. 5d), whose position scales nicely with that of the Cu  $\text{L}_3$  maximum. This suggests that Cu is more robust against oxidation not only in the catalyst bulk, but also in the surface.

To summarize, the analysis of the rare-earth M-edges, Cu/Fe K-edges and Cu/Fe L-edges converges towards a scenario where the electrons needed to compensate the oxygen uptake are primarily provided by  $\text{Fe}^{3+}$ , which partially oxidizes to  $\text{Fe}^{4+}$  both, in the bulk and in the particles surface. Interestingly, the  $\text{Fe}^{4+}$  electronic configuration ( $t_{2g}^3 e_g^1$ ) features the  $e_g^1$  filling proposed by Suntivich *et al.* as optimal for the OER activity in perovskite oxides.<sup>1</sup>

#### 2.4. Electronic structure close to the Fermi level: bulk *versus* surface

After addressing the impact of the O incorporation on the Fe and Cu 3d electron filling and its link to the OER activity, we

focus on the modifications of the electronic structure near the Fermi level  $E_F$ . The occupied and unoccupied density of states (DOS) near  $E_F$  determine not only the gap, directly linked to the conductivity, but also the adsorption interaction and the electron exchange rate between the OER reaction intermediates and the catalysts surface. To access these states we employ here XAS at the O K-edge that we combine DFT+U *ab initio* calculations.

**O K-edges.** According to the electric dipole selection rules, the main contribution to O K-edges comes from the excitation of O 1s electrons into empty O states of 2p symmetry. However, it is also possible to obtain information about the density of empty 3d states of the TM cations thanks to their hybridization with the O 2p states. In perovskite oxides these states usually appear in the lowest energy part of the spectra, and reflect the O 2p weight in states of predominantly 3d character.<sup>51</sup>

Fig. 6 shows the normalized O K-edges of our  $\text{RBaCuFeO}_{5+\delta}$  layered perovskites measured using the total fluorescence yield (TFY) and TEY detection modes (ESI<sup>†</sup>). Since TFY can be considered a bulk probe whereas TEY is more sensitive to the particle's surface, the use of both detection modes allows for a depth-profile analysis of the  $\text{RBaCuFeO}_{5+\delta}$  particles. By comparing the two sets of data, we note that the pre-edge intensities of all samples (shaded region) are systematically higher in the TFY spectra. Moreover, the pre-edge shapes measured using the two detection techniques are very similar in the samples with  $\delta = 0$ , but notoriously different in the O-rich samples. Since the pre-edge structures of TM oxides reflect the CEF splitting of the 3d orbitals,<sup>51</sup> the similar TFY and TEY pre-edge shapes of the compounds with  $R = \text{Lu}$  to  $\text{Eu}$  ( $\delta = 0$ ) suggest a common TM environment in the bulk and the surface. The lower intensity of the TEY pre-edges suggests nevertheless a reduced O 2p-TM 3d surface hybridization, possibly due to slightly longer TM-O distances and/or smaller TM-O-TM angles in the  $\text{TMO}_5$  pyramids compared with the bulk. For the samples with  $R = \text{Nd}$ ,  $\text{Pr}$  and  $\text{La}$  ( $\delta > 0$ ), the different shapes of the TFY and TEY pre-edges suggest in contrast that existence of an important surface reconstruction happening exclusively in these O-rich materials.

**DFT calculations: O-poor  $\text{RBaCuFeO}_{5+\delta}$  samples ( $\delta = 0$ ).** To rationalize these observations we used fully-relaxed *ab initio* DFT calculations, whose details are described in the Materials and Methods section (ESI<sup>†</sup> Fig. S10–S13). The calculations were performed for the bulk materials, but as we show later, they are also a good starting point to understand the catalyst's surface. As shown in ref. 51 DFT-calculated density of empty states are in general quite close to the experimentally measured O K-edges. This is illustrated in Fig. 7a and b, where we compare the low-energy part of the  $\text{LuBaCuFeO}_5$  O K-edges measured using the TFY mode with the bulk DFT calculation. The calculated DOS confirms that the structures below  $\approx 531$  eV correspond to O states hybridized with empty Fe and Cu 3d states. Moreover, the main contribution to the TM empty DOS comes from the Fe 3d orbitals (Fig. 7b). This is consistent with nominal Fe (+3) and Cu (+2) oxidation states, with five and one 3d holes respectively. Moreover, their energies reflect their CEF



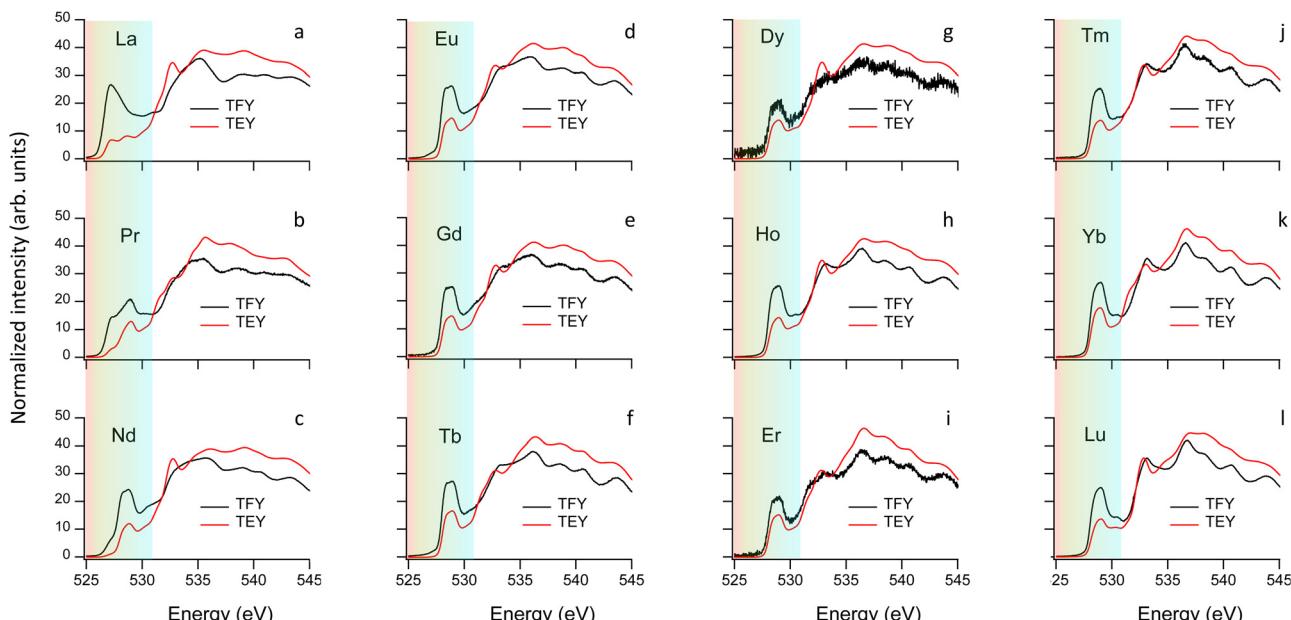


Fig. 6 O K-edges of  $\text{RBaCuFeO}_{5+\delta}$  layered perovskites measured using the TFY and TEY modes. The color-shaded areas indicate the energy range associated to empty 3d TM states hybridized with the O 2p states.

splitting in square-pyramidal coordination, which is significantly different from the familiar  $t_{2g}-e_g$  splitting observed in octahedral coordination. The main difference is the strong stabilization of the  $d_{z^2}$  orbital (Fig. 1b), which has now energies close to that of the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals. In  $\text{LuBaCuFeO}_5$ , this gives rise to an intense, broad absorption maximum labelled “A” and centered around  $\approx 529$  eV that corresponds to transitions into four of the five half-occupied  $\text{Fe}^{3+}$  3d orbitals ( $d_{z^2}$ ,  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$ ), plus the only half-occupied  $\text{Cu}^{2+}$  3d orbital  $d_{x^2-y^2}$  (Fig. 7c and d). The transition into empty  $\text{Fe}$  3d- $d_{x^2-y^2}$  states labelled “B” appears about 1.5 eV higher ( $\approx 530.5$  eV), and has a considerably lower intensity consistent with the smaller number of accessible empty states.

For the remaining  $\text{RBaCuFeO}_5$  materials with  $\delta = 0$  ( $\text{R} = \text{Lu}$  to  $\text{Eu}$ ) the agreement between the measured pre-edges (Fig. 6) and the calculated DOS (Fig. S12, ESI<sup>†</sup>) is also remarkably good. Moreover, the calculations are able to reproduce the energies and relative intensities of the “A” and “B” features in both, the TFY and the TEY spectra, as well as their practical invariance with  $R_{\text{ionic}}$ . This supports our initial guess concerning the absence of significant differences between bulk and surface 3d crystal field splittings for these materials, suggestive of a surface Cu/Fe environment quite similar to that of the particle’s bulk.

**DFT calculations: O-rich  $\text{RBaCuFeO}_{5+\delta}$  samples ( $\delta > 0$ ).** For the materials with oxygen excess, a new feature labeled “C” and centered around  $\approx 527$  eV starts to become evident for  $\text{R} = \text{Nd}$  in both, the TFY and the TEY spectra. It grows continuously with  $\delta$  in both sets of data, albeit at a much faster rate in the bulk-related TFY spectra. Its intensity is particularly large for the TFY pre-edge of the La sample, where it dominates the low energy part of the unoccupied DOS. Since this feature is clearly

linked to the incorporation of extra O in the structure we performed two additional sets of (bulk) DFT calculations for the oxygen-rich samples using two additional O stoichiometries ( $\text{RBaCuFeO}_{5.5}$  and  $\text{RBaCuFeO}_6$ ), the last one representing the end case of the O incorporation (Fig. S10, S13 and S14, ESI<sup>†</sup>).

The agreement between theory and experiment is illustrated in Fig. 7e and f, showing a comparison between the observed TFY pre-edge of the Pr sample and the DOS calculated for  $\text{PrBaCuFeO}_{5.5}$ . Besides reproducing the energies and approximate relative intensities of the different pre-edges features, the calculation allows also to identify the “C” feature. As shown in Fig. S14 (ESI<sup>†</sup>), the appearance of these states upon O incorporation results in a drastic reduction of the gap, which disappears already for  $\delta = 0.5$ . Moreover, the DFT-calculated DOS also reveals the appearance of additional O 2p hole states at energies very close to those of the Fe 3d- $d_{x^2-y^2}$  orbitals (B-feature). This increases substantially the Fe 3d-O 2p intermixing, in excellent agreement with the sharp rise of the hybridization parameter  $W$  for the materials with  $\delta > 0$  (Fig. 3a). Another interesting observation is that the overlap between the 3d- $d_{x^2-y^2}$  empty states and new O 2p holes is much larger for Fe than for Cu. This, together with the additional contribution to the O 2p-Fe 3d- $d_{z^2}$  hybridization from the “C” feature is consistent with the preferential oxidation of  $\text{Fe}^{3+}$  into  $\text{Fe}^{4+}$  upon oxygen incorporation, in agreement with the conclusions inferred from the analysis of the K and L TM edges.

For the O-rich materials, we note that the agreement between the measured TFY pre-edge intensities and the calculated DOS is less good than in the case of the O-poor compounds, in particular for  $\text{R} = \text{La}$ . This could arise from the difference between the actual O content and the  $\delta$  values employed in the calculations, but also from the difficulty of



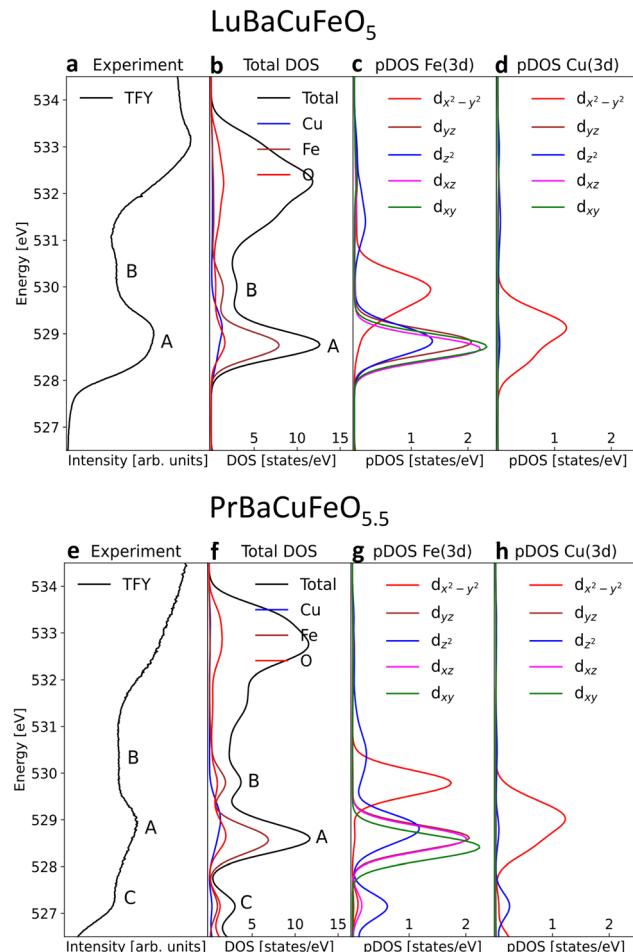


Fig. 7 Comparison between the O K-edges measured in TFY mode and the DOS from DFT calculations together with the Fe, Cu and O partial-DOS and the contributions of the different empty Fe and Cu 3d orbitals. (a)–(d) LuBaCuFeO<sub>5</sub>. (e)–(h) PrBaCuFeO<sub>5.5</sub>.

implementing in DFT complex O vacancy distributions and R/Ba intermixing patterns while keeping reasonable computing times. A comparison between the experimental PFY O K-edges and the calculated DOS indicates nevertheless that the supercells used in this study (Fig. S10, ESI<sup>†</sup>) are a good compromise that allows to capture the main features of the PFY pre-edges of the O-rich samples. This concerns the energies of the “A”, “B” and “C” features, their approximate relative intensities, as well as the progressive metallization of RBaCuFeO<sub>5+δ</sub> layered perovskites upon O incorporation into the lattice.

We address now the possible origins of the strong differences between the TFY and TEY pre-edges observed in the O-rich samples. The most salient among them is the growth rate of the “C” feature with  $\delta$ , much faster in the bulk TFY than in the surface-related TEY spectra. Since this feature is related to the O 2p–Fe 3d<sub>z2</sub> hybridization, we can tentatively assign the lower intensity in the TEY pre-edges to an oxygen depletion in the surface. However, it could also arise from a structural rearrangement in the particle’s surface involving a decrease of the O 2p–Fe 3d<sub>z2</sub> overlap. An example of the last possibility

was recently provided by our recent study on the isostructural layered cobaltite PrBaCo<sub>2</sub>O<sub>5.43</sub>, where the existence of a surface reconstruction with less efficient Co 3d–O 2p overlap was suspected from the differences between the TFY and TEY O K-edge spectra and further confirmed by high-resolution scanning transmission electron microscopy (STEM) measurements.<sup>30</sup> This last technique revealed important displacements of the Co sites with respect to the bulk positions in a thin surface layer ( $\sim 2$  unit cells) compatible with a reduced Co 3d–O 2p hybridization. Given the absence of high-resolution STEM measurements for our O-rich samples we cannot unambiguously claim a similar origin for the TFY–TEY differences based in our O K-edge data alone. However, given the common layered perovskite structure, similar O content, and strong similarities between the bulk and surface O K spectra of PrBaCo<sub>2</sub>O<sub>5.43</sub> and LaBaCuFeO<sub>5.49</sub>, it seems reasonable to assume that such possibility is not unlikely.

Besides Co displacements, STEM measurements also revealed the existence of Ba depletion in the PrBaCo<sub>2</sub>O<sub>5.43</sub> particles surface. Ba segregation has already been reported in the literature for long, high-temperature annealing processes on Ba containing perovskites with  $\delta > 0$ ,<sup>52</sup> and given the synthesis procedure employed in this study, it could also happen in our samples. In order to check this possibility we measured the Ba M<sub>5,4</sub> absorption edges, whose main contribution comes from the excitation of electrons from the transition of electrons from the spin-orbit-split levels 3d<sub>5/2</sub> and 3d<sub>3/2</sub> into empty states of 4f symmetry. The Ba M<sub>5,4</sub> spectra recorded using the surface-sensitive TEY mode, are shown in Fig. S15a (ESI<sup>†</sup>) and look very similar to those reported in compounds containing Ba<sup>2+</sup>.<sup>53</sup> Moreover, in contrast with the behaviour observed in the L<sub>3,2</sub> Fe edges (Fig. 5), the M<sub>5,4</sub> lines change very little with the R ionic radii, without appreciable discontinuities in the M<sub>5</sub> and M<sub>4</sub> maxima at the setup of the oxygen uptake (Fig. S15b, ESI<sup>†</sup>). This observation suggests that the surface reconstruction of the O-rich samples does not involve significant changes in the Ba coordination, which would remain similar to that of the samples with  $\delta = 0$ .

#### DFT calculations: band gap and O 2p valence band centroid.

The calculated DOS provides also an estimation of the band gap  $E_{\text{gap}}$ , shown schematically in Fig. 8a. For the samples with  $\delta = 0$  (R = Lu to Eu)  $E_{\text{gap}}$  takes values close to 2.2 eV, typical of semiconductors and compatible with the measured resistivity  $\rho = 1/\sigma$  values (Fig. 8b). Moreover, its smooth decrease for increasingly larger R ionic radii is consistent with the practical invariance of  $\rho$  and the hybridization parameter  $W$  (Fig. 3a) in these materials. For the O-rich samples (R = Nd, Pr, La) the resistivity decreases very fast upon O incorporation, reaching values more than six orders of magnitude lower typical of metals in the case of R = La. This trend is nicely reproduced by DFT calculations, where the appearance of new hole states for growing  $\delta$  values leads to the progressive reduction of the gap (Fig. S14, ESI<sup>†</sup>), fully closed in the RBaCuFeO<sub>6</sub> materials (white markers in Fig. 8b).

A further parameter delivered by DFT calculations is the valence O 2p band centroid  $E_{\text{cent}}$  relative to the Fermi level (black vertical arrow in Fig. 8a), reported to positively correlate

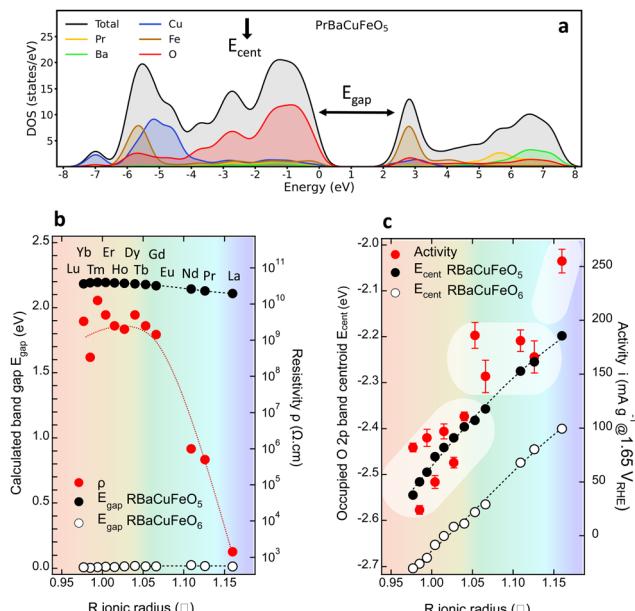


Fig. 8 (a) Calculated DOS for PrBaCuFeO<sub>5</sub> showing the location of the valence band O 2p centroid  $E_{\text{cent}}$  and the band gap  $E_{\text{gap}}$ . (b) Left axis: calculated  $E_{\text{gap}}$  for the RBaCuFeO<sub>5</sub> and RBaCuFeO<sub>6</sub> bulk materials. Right axis: experimental resistivity. (c) Comparison between the changes in the experimental OER activity upon R-cation replacement with those in the calculated valence band O 2p  $E_{\text{cent}}$  for RBaCuFeO<sub>5</sub> and RBaCuFeO<sub>6</sub>.

with the OER activity in Co-based layered perovskites RBa<sub>2</sub>Co<sub>2</sub>O<sub>5+δ</sub> with  $\delta > 0$  under the assumption that the catalyst surface is fully oxidized ( $\delta = 1$ ).<sup>15</sup> The evolution of this variable for the RBaCuFeO<sub>5+δ</sub> ferrocuprates with  $\delta = 0$  and  $\delta = 1$ , shown in Fig. 8c and Fig. S12, S13 (ESI†) indicates that, in both cases,  $E_{\text{cent}}$  approaches monotonically  $E_F$  for increasing  $R_{\text{ionic}}$  values. However, it also reveals that  $E_{\text{cent}}$  moves away from  $E_F$  by increasing the oxygen content  $\delta$ . The use of the valence O 2p band centroid as OER descriptor relies thus on whether the catalyst surface can be considered fully oxidized in all the materials under comparison.

In our RBaCuFeO<sub>5+δ</sub> samples, where the bulk O content changes between 5 (Lu to Eu) and 5.49 (La), the degree of surface oxidation can be assessed from the intensity of the “C” feature in the TEY spectra, which indicates the presence of O excess in the surface. This feature, absent in the samples with  $\delta = 0$ , is clearly present in TEY spectra of the materials with R = Nd, Pr and La. Moreover, its intensity increases with  $\delta$  and is systematically lower than in the TFY spectra, which reflect the bulk O excess (always lower than 0.5). These observations are difficult to conciliate with a common, fully oxidized surface ( $\delta = 1$ ). The proposed positive correlation between OER activity and  $E_{\text{Op}}$  is thus not expected to apply to our samples, at least in their pristine form. The confirmation of this guess is illustrated in Fig. 8c, where the correlation between OER activity (red markers) and  $E_{\text{cent}}$  is positive only for the samples with the same O content (R = Lu to Eu,  $\delta = 0$ ). For R = Nd, Pr and La the OER activity increases continuously but  $E_{\text{cent}}$  decreases due to their increasingly large O content. The OER- $E_{\text{cent}}$  correlation is

thus negative. Operando or post-operando O K-edge measurements will be necessary to assess whether the surface oxygen content is modified after the OER process with respect to the pristine materials.

## 2.5. Role of 4f electrons

Traditionally, the role of the A cations in the OER process has been considered marginal, and the few studies suggesting their involvement for some perovskite oxides have only been reported recently.<sup>54</sup> In the particular case of RBaCuFeO<sub>5+δ</sub> layered perovskites, an active participation of the R cations, with localized 4f electrons contributing very little to the DOS close of the Fermi level (Fig. S12, ESI†) seems unlikely. The alternating behaviour of the activity with the parity of the 4f electron count observed in the compounds with  $\delta = 0$  (Fig. 1c) is thus unexpected, and suggests a possible impact of the ground state of the R<sup>3+</sup> cations (a singlet and a Kramers doublet for even and odd 4f electrons counts, respectively). Additional support in this sense is provided by the loss of the 4f electron count alternation at the setup of the extra oxygen uptake (R = Gd), where the increased structural disorder and inhomogeneity are expected to modify the symmetry of the R<sup>3+</sup> cation ground state. Finding what is the exact role of the 4f electrons in the OER activity of the O-poor materials is nevertheless beyond the scope of this study and will require additional experimental and theoretical work.

## 2.6. Intrinsic OER activity: comparison between LaBaCuFeO<sub>5+δ</sub> and PrBaCo<sub>2</sub>O<sub>5+δ</sub>

The use of well-crystallized samples prepared by solid-state synthesis was necessary to obtain PND data with sharp Bragg reflections suitable for a detailed structural analysis. However, it was clearly detrimental for the electrochemical performance due to their large particle sizes. To evaluate the impact of this variable we prepared a nanometer-sized LaBaCuFeO<sub>5+δ</sub> sample using flame-spray synthesis, an easily scalable synthetic method proved to be very efficient in the large production of perovskites nanopowders.<sup>13,55</sup> The conditions used for the synthesis guaranteed a good compromise between particle size (Fig. S3 and Table S3, ESI†) and sample purity, with only minor amounts of precursors still present in the final sample (Fig. S16a, ESI†). As shown in Fig. 9 and Table S1–2 (ESI†), reducing the average LaBaCuFeO<sub>5+δ</sub> particle size from the micro to the nano-range increases the OER gravimetric activity at 1.65 V<sub>RHE</sub> by a factor of ~5. This increase occurs in spite of an eight orders of magnitude decrease in conductivity due to the increased grain-boundaries resistance (Table S1, ESI†), and the presence of secondary phases in the catalyst powder, which result in the underestimation of the nano-electrocatalyst activity.

Next, we compared the intrinsic (*i.e.*, surface-normalized activity) of our nano-sample with that of nano-sized PrBaCo<sub>2</sub>O<sub>5+δ</sub> synthesized using the same technique and measured at the same pH (=13).<sup>13</sup> Normalization to the BET-measured surface area (5.8 m<sup>2</sup> g<sup>-1</sup>) gives an OER activity of 0.0047 mA cm<sup>-2</sup> at 1.60 V<sub>RHE</sub> for the LaBaCuFeO<sub>5+δ</sub> nanopowder, a value ≈ 25 times



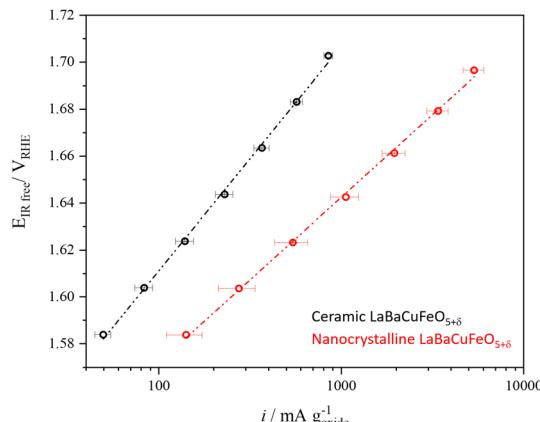


Fig. 9 Comparison between the gravimetric activity of the ceramic and nanocrystalline  $\text{LaBaCuFeO}_{5+\delta}$  samples.

smaller than the activity reported for  $\text{PrBaCo}_2\text{O}_{5+\delta}$  nanoparticles at the same  $V_{\text{RHE}}$  ( $0.12 \text{ mA cm}^{-2}$ ).<sup>13</sup> The activity of the ferrocuprate is also lower than the value reported for  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  thin films at the same pH and  $V_{\text{RHE}}$  ( $\approx 0.1 \text{ mA cm}^{-2}$ ),<sup>56</sup> although in this case a comparison is less straightforward due to the different purity and geometry of both materials. Given the absence of cobalt and the exploratory nature of our study, the results obtained for the  $\text{LaBaCuFeO}_{5+\delta}$  nanopowder are nevertheless encouraging, and call for additional investigations aimed at improving this promising result.

### 3. Discussion and conclusions

In this study, we have investigated the potential of the layered perovskite family  $\text{RBaCuFeO}_{5+\delta}$  as Co-free OER catalysts, with cheap, abundant transition metals in the B-positions. Our OER activity measurements reveal a complex behaviour along the 4f series, with no direct correlation with the R ionic radius, the electric conductivity or the valence O 2p band centroid. To rationalize these results we investigated in detail the changes in the crystal and electronic structures using a combination of *ab initio* calculations and advanced neutron and X-ray synchrotron techniques. The behaviour of the OER activity along the 4f series was then contrasted with that of different structural and electronic parameters proposed as OER descriptors in the recent literature.

Our combined analysis reveals a positive impact of the oxygen excess ( $\delta > 0$ ) in the conductivity, which leads to the preferential oxidation of  $\text{Fe}^{3+}$  into  $\text{Fe}^{4+}$  while keeping the  $\text{Cu}^{2+}$  valence nearly unchanged. The creation of  $\text{Fe}^{4+}$  sites upon oxygen incorporation results in a sharp rise of the Fe–O hybridization and in the creation of new hole-states in the gap. The combined effect of these two mechanisms is at the origin of the abrupt increase of the electric conductivity, which remains nearly constant in the O-poor samples ( $\delta = 0$ ). Interestingly, growing  $\sigma$  values do not grant a simultaneous increase of the OER activity, which requires also sufficient weakly bound oxygen and a distribution of oxygen vacancies that ensures enough oxygen diffusion channels in the catalysts bulk.

In  $\text{RBaCuFeO}_{5+\delta}$  layered perovskites, the R/Ba alternation restricts the oxygen vacancies to the R-planes due to the stronger affinity of  $\text{Ba}^{2+}$  for high oxygen coordination compared to that of the R<sup>3+</sup> cations. The incorporation of weakly bonded oxygen to these planes opens a new electronic conduction channel along the *c*-axis, and was also expected to enable O diffusion in the R-layers. The shape of the thermal ellipsoids suggest however that this extra oxygen remains static as long as the R/Ba order along the *c*-axis is preserved. Interestingly, a certain degree of Ba/R intermixing (observed here only for R = La) has a huge impact in the shape of the O thermal ellipsoids, which is now compatible with the existence of O 2D diffusion *both*, in the La and in the Ba planes. The presence of some low-coordinated La cations in the Ba layers allows indeed the creation of O vacancies also in these layers. Moreover, it homogenizes the interatomic distances and angles (Fig. 2), resulting in a smoother potential landscape that lowers the energy barrier for O jumps and facilitates the setup of O diffusion.

It is worth mentioning that our structural data alone do not prove the presence of O diffusion in  $\text{LaBaCuFeO}_{5.45}$ . However, they strongly support it based on similar observations in other ionic conductors.<sup>40,57,58</sup> Incidentally,  $\text{LaBaCuFeO}_{5.45}$  shows also the best electrochemical performance of this study. It is thus tempting to make the link between O diffusion in the catalyst's bulk and OER activity, a link that, at least for this material, suggests the participation of the lattice oxygen in the OER process (LOER).<sup>3,30,59</sup>

A further interesting result of this investigation is the observation of an important reconstruction of the catalysts surface exclusively in the O-rich samples. For the O-poor materials ( $\delta = 0$ ), the close similarity between the O K-edges measured using the TFY and TEY modes indicates only minor differences between the catalyst's bulk and surface. In contrast, the pronounced differences observed in the O rich samples indicate the existence of major structural changes involving either O depletion, and/or a huge decrease of TM–O hybridization. Intriguingly, our data do not provide any clear evidence for modification of the Ba environment in particle's surface by increasing the O content. A possible reason could be a preference for surface terminations containing the R-cations. The  $\text{RBaCuFeO}_{5+\delta}$  oxides are indeed layered materials with a preference for surface terminations perpendicular to the *c* axis. Since the strongest bonds correspond to the Cu–O/Fe–O layers, the planes containing the R-cations are prominent candidates due to the reduced number of R–O bonds compared with the Ba–O planes. Interestingly, such a scenario could bring the 4f orbitals close to OER intermediates, giving some hints to understand the intriguing alternation of the OER activity with the 4f electron count. Experiments on  $\text{RBaCuFeO}_{5+\delta}$  thin films with different surface terminations could help to establish whether this is the case in the  $\text{RBaCuFeO}_{5+\delta}$  family.

Since the best OER performance of this study corresponds to  $\text{LaBaCuFeO}_{5.45}$ , which has lost some of its layered character due to the partial La/Ba intermixing, a pertinent question is whether a cubic material with the same composition (including



O content) but perfectly random A-site disorder would be a more performant electrocatalyst. Our results suggest that some layered character, even if it is reduced by the R/Ba intermixing, helps to create a stack of physically separated R–O and Ba–O planes with a smooth potential landscape for O ionic diffusion, seemly advantageous for a high OER activity. This situation is not found in cubic materials, where O diffusion paths can be more intricate. The better suitability of the layered perovskite framework for the OER process has also been proposed in some recent studies, and attributed to the optimal position of the calculated O 2p valence band centroid  $E_{\text{cent}}$  with respect to the Fermi level, close to  $E_F$  but more distant than in the case of 3D perovskites. In the case of the  $\text{RBaCuFeO}_{5+\delta}$  family, the highest OER activity corresponds to R = La, the materials where  $E_{\text{cent}}$  is the most distant from  $E_F$ , and the only one that is pseudocubic. The proposed trend is thus not verified in our samples. A possible reason for the disagreement is that the O 2p band centroid calculations in ref. 15 were performed assuming a fully oxidized ( $\delta = 1$ ) catalyst surface in the materials under comparison, a condition that is not verified in our samples, at least in their pristine form. Operando or post-operando O K-edge measurements will be necessary to assess whether the surface oxygen content is modified after the OER process with respect to the pristine materials.

As a concluding remark, we would like to point out that the results presented in this study allowed to identify several strategies that could help to design a Co-free layered perovskite with improved OER performance. One of the most critical variables appears to be the choice of the A and A' cations, whose ionic radii should be close enough to allow intermixing but different enough to preserve some degree of layered character.  $\text{La}^{3+}/\text{Ba}^{2+}$  and perhaps  $\text{Pr}^{3+}/\text{Ba}^{2+}$  look as the most promising candidates, but other  $\text{R}^{3+}$ -cations can be also suitable using synthetic techniques favoring an intimate mixing of the material's precursors. Concerning B-cations, our XAS data point towards a large number of empty 3d orbitals, in particular those enabling Sigma-bonding and thus a higher degree of TM 3d–O 2p hybridization. Configurations with a large number of  $e_g$  holes such as  $t_{2g}^3 e_g^1$  ( $\text{Fe}^{4+}$ ,  $\text{Mn}^{3+}$ ) or  $t_{2g}^6 e_g^1$  ( $\text{Ni}^{3+}$ ,  $\text{Co}^{2+}$ ) appear thus as ideally suited. If we exclude  $\text{Co}^{2+}$ , as well as  $\text{Ni}^{3+}$  that may require the use of high O pressure,<sup>60</sup> possible candidate materials could be the solid solutions  $\text{LaBaCu}_{1-x}\text{Mn}_x\text{FeO}_{5+\delta}$  ( $\delta < 0.5$ ) and  $\text{LaBaCu}_{1-x}\text{Fe}_x\text{O}_{5+\delta}$  ( $\delta > 0.5$ ) where the stability of the  $\text{Cu}^{2+}$  oxidation state is expected to favour large amounts of Fe and Mn with electronic configurations close to  $e_g^1$ . An additional strategy could be to determine, for each candidate material, the optimal oxygen content. In this case, it will be important to avoid “magical” O contents such as  $\text{O}_{5.5}$ , prone to O vacancy order and electronic localization.<sup>61</sup>  $\text{LaBaCuFeO}_{5.49}$ , the material with the best figures of merit of our study, is close to this composition, but contrarily to the A-site ordered cobaltite  $\text{PrBaCo}_2\text{O}_{5.48}$ ,<sup>30</sup> O-vacancy order was not observed, most probably because of the huge structural inhomogeneity caused by the La/Ba disorder. The growth of layered perovskites in thin film form, which allows obtaining extremely pure materials with large active surfaces, could also be a possible approach.<sup>62</sup>

Interestingly, previous studies on the layered Co perovskite  $\text{PrBaCo}_2\text{O}_{5+\delta}$  grown as epitaxial thin films indicate that, as reported in this study, structural disorder – and in particular A-site intermixing – is beneficial for the OER activity.<sup>63</sup> A further approach could be to exploit the multiferroic nature of some such materials,<sup>64</sup> which has been shown to be beneficial for the catalytic activity in some recent studies.<sup>65–67</sup>

To summarize, we have experimentally investigated the potential of  $\text{RBaCuFeO}_{5+\delta}$  perovskites as Co-free OER catalysts. Our detailed structural characterization constitutes one of the few attempts to rationalize electrochemical properties in terms of TM–O interatomic distances, TM–O–TM angles, O content and chemical disorder and mean-square displacements, which were determined in this study with great precision. By combining these data with the results of X-ray spectroscopies and DFT calculations we could identify the critical structural and electronic variables leading to high OER catalytic performance, which can be exploited for the design of other Co-free layered perovskites. Moreover, our study revealed  $\text{LaBaCuFeO}_{5+\delta}$  as a new promising OER catalyst candidate that can be industrially produced in nanocrystalline form. Altogether, our results provide additional support to the layered perovskite structure as a promising structural framework to search for OER catalysts, and could accelerate the discovery of Co-free materials with optimal properties for electrochemical water splitting and  $\text{H}_2$  production.

## Author contributions

Elena Marelli (lead author): formal analysis, investigation, methodology, visualization, writing – original draft. Jike Lyu (equal contribution): formal analysis, investigation, methodology, visualization, writing – original draft. Mickaël Morin (supporting author): investigation, methodology, writing – reviewing & editing. Maxime Leménager (supporting author): investigation, methodology, writing – reviewing & editing. Tian Shang (supporting author): investigation, methodology, writing – reviewing & editing. Sena Yüzbasi (supporting author): investigation, methodology, writing – reviewing & editing. Dino Aegeuter (supporting author): investigation, methodology, writing – reviewing & editing. Jinzhen Huang (supporting author): investigation, methodology, writing – reviewing & editing. Nieli D. Daffé (supporting author): investigation, methodology, writing – reviewing & editing. Adam H. Clark (supporting author): investigation, methodology, software, writing – reviewing & editing. Denis Sheptyakov (supporting author): investigation, methodology, writing – reviewing & editing. Thomas Graule (supporting author): validation, writing – reviewing & editing. Maarten Nachtegaal (supporting author): writing – reviewing & editing. Ekaterina Pomjakushina (supporting author): validation, writing – reviewing & editing. Thomas J. Schmidt (supporting author): writing – reviewing & editing. Mattias Krack (corresponding author): formal analysis, investigation, methodology, software, visualization, writing – reviewing & editing. Emiliana Fabbri (corresponding author): conceptualization, funding acquisition, project administration, methodology, supervision, validation,



writing – reviewing & editing. Marisa Medarde (corresponding author): conceptualization, funding acquisition, project administration, methodology, investigation, formal analysis, supervision, writing – original draft.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work is based on experiments performed at the Swiss spallation neutron source SINQ (HRPT diffractometer), and the Swiss Light Source (SuperXAS and Xtreme beamlines) at the Paul Scherrer Institute, Villigen, Switzerland. It was supported by the Swiss National Science Foundation (Grants No. 200021-141334/1, 200021-141334/2 and 206021-139082), and by the PSI internal funding instrument CROSS. We acknowledge access to Piz Daint at the Swiss National Supercomputing Centre, Switzerland under PSI's share with the project ID psi01.

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