



# Effect of Cu doping on $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$ perovskites for solid oxide fuel cells: A first-principles study



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## HIGHLIGHTS

- $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  was simulated using first-principles.
- Thermodynamic stability decreases with the incorporation of Cu into the structure.
- Oxygen vacancy formation and diffusion barriers decrease with the Cu-substitution.
- Copper inclusion in the structure brings the O p-band closer to the Fermi level.
- p-band proximity to Fermi level promotes an increase of the ORR activity.

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## ABSTRACT

Nowadays a rational design of solid oxide fuel cells (SOFCs) cathodes is possible thanks to first-principles calculations based on density functional theory (DFT). We study the effect of Cu-doping in the bulk properties for the perovskite  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  (with  $x = 0, 0.25$  and  $0.50$ ) and correlate the results with previous experimental characterization. Bulk properties such as geometric structure, charge analysis, thermodynamic stability, vacancy formation energy, oxygen diffusion and electronic structure were studied in detail to provide an explanation of the oxygen reduction reaction (ORR) activity enhancement with Cu-doping. The results obtained here, using GGA+U, demonstrate the first-principles approach gives useful information that allows the prediction and explanation of experimental characterizations.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) are efficient devices for power generation with a low environmental impact and the advantage of working with different fuels as hydrogen, natural gas, and renewable fuels [1]. One of the most important research challenges for SOFCs commercialization is the reduction of the operation temperature from the high temperature range (800–1000 °C) to the intermediate temperature range (500–700 °C) [2]. The operation in the intermediate temperature (IT-SOFCs) reduces the manufacturing costs and materials compatibility problems and improves the long term stability and durability. The cathode polarization represents one of the most important energy losses in the SOFCs and this becomes more important at lower operation

temperatures [3].

One strategy to improve the cathode performance below 800 °C is use a mixed ionic-electronic conductors (MIECs) such as  $(\text{A}_{1-x}\text{Sr}_x)(\text{B}_{1-y}\text{B}'_y)\text{O}_{3-\delta}$  (with  $\text{A} = \text{Ba}$  or  $\text{La}$ ;  $\text{B}$  or  $\text{B}' = \text{Mn}$ ,  $\text{Fe}$  or  $\text{Co}$ ). The possibility for transport oxygen ion and electrons through a simple-phase extends the number of active sites for the oxygen reduction reaction (ORR) and enhance the cathode performance [3,4]. It has been reported that Co-based cathode materials exhibit better performance than Mn-based ones [5]. The cobalt-based perovskites  $\text{Ba}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  (BSCF) [2,6,7] and  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  (LSCF) [8,9] have been extensively investigated due to their low polarization losses ascribed to its rapid oxygen bulk diffusion rate and surface exchange kinetics. Nevertheless, two major drawbacks prevent the use of cobalt-based perovskites in commercial application: (i) a large thermal expansion coefficient (TEC) compared to the commonly used electrolytes (GDC or YSZ) that induces the fracture of the cell during operation cycles and (ii) the degradation of the cathode activity at high temperatures.

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Recently, has been a tremendous growth on the cathode design using density functional theory (DFT) calculations [10–13]. Ab initio calculations using DFT are important to resolve atomistic details that are not easily obtained experimentally such as the oxygen incorporation reaction, transition states in chemical reactions or diffusion, oxygen adsorption energies, point defect concentrations and other fundamental properties. (La,Sr)MnO<sub>3-δ</sub> has been extensively studied to determine the most probable oxygen incorporation mechanism, this includes the energetics calculation of oxygen vacancy, probable surface terminations, adsorption energies, dissociation energies and oxygen transport [13–16]. Cobalt-based perovskites also have been studied by several authors using ab-initio methods due to their fast oxygen reduction kinetics and ionic transport [17–22].

The new trend in cathode design is to develop cobalt-free materials with superior activity for ORR. Fe-based perovskites demonstrate to be more stable than cobalt containing perovskites and we are using Ba<sub>0.5</sub>Sr<sub>0.5</sub>FeO<sub>3-δ</sub> as base material to develop new cathodes. Due to the low oxygen reduction kinetics of Ba<sub>0.5</sub>Sr<sub>0.5</sub>FeO<sub>3-δ</sub> it is desirable the Fe substitution using a transition metal to facilitate the oxygen inclusion and ionic transport. Recently, we report for the composition Ba<sub>0.5</sub>Sr<sub>0.5</sub>Fe<sub>0.8</sub>Cu<sub>0.2</sub>O<sub>3-δ</sub> a low area specific resistance (ASR) of 0.035 Ω cm<sup>2</sup> at 700 °C characterized by electrochemical impedance spectroscopy (EIS) [23], which is comparable to the measured ASR values from cobalt-based perovskites [5]. In comparison with Ba<sub>0.5</sub>Sr<sub>0.5</sub>FeO<sub>3-δ</sub> the Cu-doped structure smoothly increases the conductivity from a maximum of 42 S cm<sup>-1</sup> at 600 °C for Ba<sub>0.5</sub>Sr<sub>0.5</sub>FeO<sub>3-δ</sub> [24] to a maximum of 60 S cm<sup>-1</sup> at 600 °C for Ba<sub>0.5</sub>Sr<sub>0.5</sub>Fe<sub>0.8</sub>Cu<sub>0.2</sub>O<sub>3-δ</sub> [25]. Therefore the ORR activity is substantially higher in the cathodes containing copper and the small change in the electronic conductivity does not explain this behaviour.

In this work we calculate by means of ab initio DFT the effect of Cu-doping on the Ba<sub>0.5</sub>Sr<sub>0.5</sub>FeO<sub>3-δ</sub> perovskite to understand why the ORR activity is enhanced. To analyze the effect of Cu-doped perovskite we calculate different composition and vacancy contents according to the formula Ba<sub>0.5</sub>Sr<sub>0.5</sub>Fe<sub>1-x</sub>Cu<sub>x</sub>O<sub>3-δ</sub> with x = 0, 0.25, 0.5 and δ = 0.125, 0.25. The geometric structure, charge analysis, thermodynamic stability, vacancy formation energy, oxygen diffusion and electronic structure where studied in detail. To the best of our knowledge, we report here the first theoretical study of Ba<sub>0.5</sub>Sr<sub>0.5</sub>Fe<sub>1-x</sub>Cu<sub>x</sub>O<sub>3-δ</sub> perovskites that evaluate the effect of Cu-doping as a strategy for obtain new IT-SOFCs cathodes.

## 2. Computational

Spin polarized DFT calculations were performed with the Vienna Ab-initio Simulation Package (VASP) [26–29] using a plane-wave basis set, the GGA-PBE exchange-correlation functional [30,31], and the projector-augmented wave (PAW) method [32,33]. We used PAW potentials for Sr, Ba, Fe, Cu and O with 10 (4s<sup>2</sup> 4p<sup>6</sup> 5s<sup>2</sup>), 10 (5s<sup>2</sup> 5p<sup>6</sup> 6s<sup>2</sup>), 8 (3 d<sup>7</sup> 4s<sup>1</sup>), 11 (3 d<sup>10</sup> 3p<sup>1</sup>) and 6 (2s<sup>2</sup> 2p<sup>4</sup>) valence electrons respectively.

All calculations were performed with a 400 eV kinetic energy cutoff for a plane wave basis set and a Monkhorst-Pack mesh with (4 × 4 × 4) k-points for a 2 × 2 × 2 supercell of the primitive perovskite structure. The convergence criteria used in all the cases was ion forces lower than 0.03 eV/Å. A more accurate description of perovskite electron structure and energies can be obtained considering the electron-correlation effects. We adopted the GGA+U approach proposed by Dudarev et al. [34] with a single effective interaction parameter U<sub>eff</sub> = U-J for atoms with 3d level electrons. The U<sub>eff</sub> for the Cu and the Fe used were 3.0 [35] and 4.0 [36] respectively.

Density functional perturbation theory (DFPT) implemented in

VASP was used to compute vibrational properties and post-processing to calculate thermodynamic properties was performed using the PHONOPY code [37,38].

Migration barriers were calculated using the climbing image nudge elastic band method (CI-NEB) and the VTTS tools from Henkelman group [39]. By starting from a well-converged initial and final state, the oxygen migration path was calculated using a set of four intermediate images and these were connected by artificial spring forces (5 eV/Å<sup>2</sup>).

## 3. Results and discussion

### 3.1. Structural models and effective charges

Perfect perovskite structure crystallizes in the cubic Pm-3m (#221) space group. In this ideal cubic perovskite structure, the B cations are 6-fold and the A cations 12-fold coordinated, with the oxygen anions. The initial structural models were constructed using the non-defective perovskite Ba<sub>0.5</sub>Sr<sub>0.5</sub>Fe<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (with x = 0, 0.25 and 0.50) and cubic supercells of size 2 × 2 × 2 (40 atoms). In previous work we determined by means of synchrotron X-ray diffraction that Ba<sub>0.5</sub>Sr<sub>0.5</sub>Fe<sub>0.8</sub>Cu<sub>0.2</sub>O<sub>3-δ</sub> has a cubic structure with cell parameter a = 3.9389 Å and the cations Ba/Sr and Fe/Cu are disordered in the A and B sites respectively [23]. To reduce the number of possible configurations of the initial lattice arrangement of the cations in the supercells we suppose that Ba/Sr alternate in the A-site. The Cu-doped perovskites have Fe or Cu cations in the B-site, so different arrangements can be constructed. Our strategy was to model all the possible B-site cation arrangement and performs a geometric optimization to calculate the most probable configuration (lower energy). For all the arrangements spin-polarized calculations were carried out using ferromagnetic (FM) and anti-ferromagnetic (AFM) ordering. The results of this calculations demonstrates that in all the configurations the FM phases are most stable than the AFM with a difference of about 1 eV/supercell (0.125 eV/unit cell). This results are in accordance with previous reports for SrFeO<sub>3</sub> [40] and (Ba,Sr)(Co,Fe)O<sub>3</sub> [17,20] that shows a more stable FM phase than AFM. The possible configurations are shown in Fig. 1 (3 configurations for x = 0.25 and 6 configurations for x = 0.50) and the total energy for the FM ordering are listed in Table 1. The most probable models are the **c** and **g** for Ba<sub>0.5</sub>Sr<sub>0.5</sub>Fe<sub>0.75</sub>Cu<sub>0.25</sub>O<sub>3</sub> and Ba<sub>0.5</sub>Sr<sub>0.5</sub>Fe<sub>0.5</sub>Cu<sub>0.5</sub>O<sub>3</sub> respectively and these structural models are used hereinafter to calculate the perovskite thermodynamic stability, oxygen vacancy formation, oxygen diffusion and electronic structure. However if we compare the total energies for different arrangements of a fixed composition, this difference is small (lower than 0.1 eV/unit cell) which is in accordance with the structural characterization that indicates a disorder in the B-site for Cu and Fe cations.

Table 1 also shows structural information of defect-free perovskites as the cell parameter and the B–O bond distances. The average cell parameters at 0K after optimization for Ba<sub>0.5</sub>Sr<sub>0.5</sub>FeO<sub>3</sub>, Ba<sub>0.5</sub>Sr<sub>0.5</sub>Fe<sub>0.75</sub>Cu<sub>0.25</sub>O<sub>3</sub> and Ba<sub>0.5</sub>Sr<sub>0.5</sub>Fe<sub>0.5</sub>Cu<sub>0.5</sub>O<sub>3</sub> are 3.8897 Å, 3.8858 Å and 3.9065 Å respectively. The experimental cell parameters obtained by X-ray diffraction at room temperature for Ba<sub>0.5</sub>Sr<sub>0.5</sub>FeO<sub>3</sub> is 3.925 Å [6] and for Ba<sub>0.5</sub>Sr<sub>0.5</sub>Fe<sub>0.8</sub>Cu<sub>0.2</sub>O<sub>3</sub> is 3.9389 Å [23], so there is a good agreement with experimental results. The geometric optimization leads to a rearrangement of the B–O bonding distance and as could be seen in Table 1, where there is a single bond distance for Fe–O. However there are two characteristic distances for Cu–O bonding that induces a octahedral distortion due to the Jahn Teller effect which is characteristic of the Cu+2 oxidation state [41].

The effective charges of the atomic species are important to understand the charge redistributions due to the oxygen vacancy

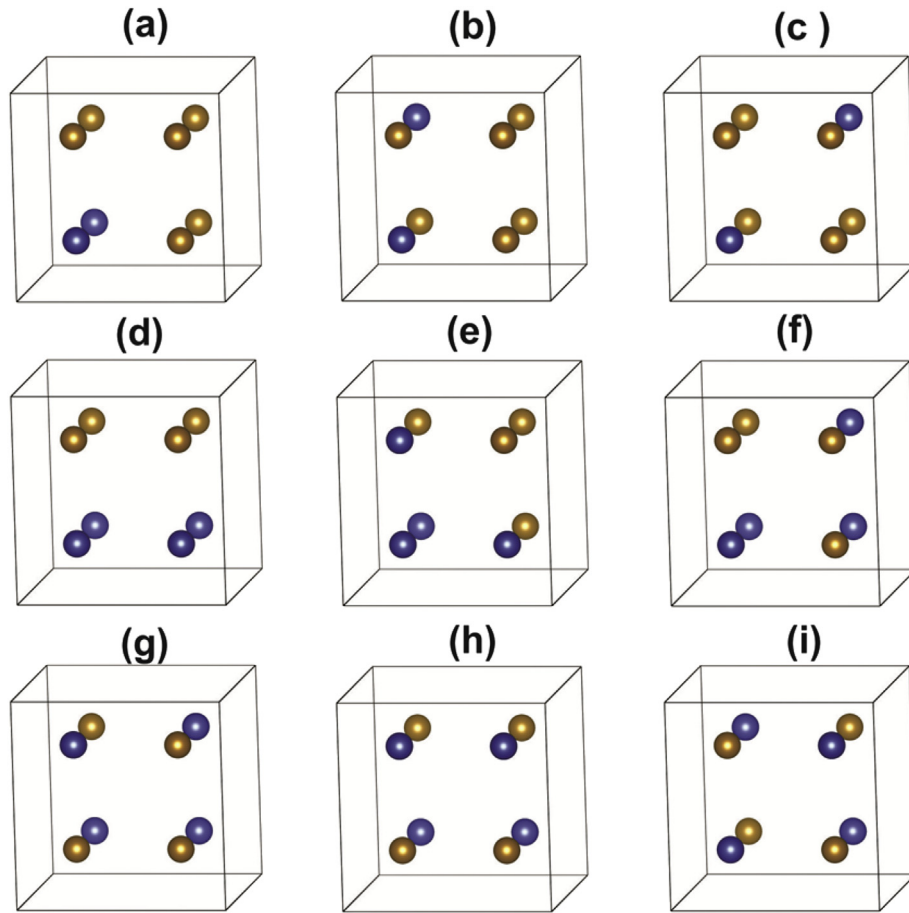


Fig. 1. Different B-cation sub-lattices for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.75}\text{Cu}_{0.25}\text{O}_3$  (a–c) and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Cu}_{0.5}\text{O}_3$  (d–i).

**Table 1**  
Structural details after geometric optimization for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Cu}_x\text{O}_3$ .

| x    | Structural model | Energy for FM conf. (eV/unit cell) | Cell parameter (Å) | d Fe–O (Å) | d Cu–O <sub>1</sub> (Å) | d Cu–O <sub>2</sub> (Å) |
|------|------------------|------------------------------------|--------------------|------------|-------------------------|-------------------------|
| 0    | –                | –32.64                             | 3.8897             | 1.945      | –                       | –                       |
| 0.25 | a                | –30.80                             | 3.8856             | 1.938      | 1.938                   | 2.028                   |
|      | b                | –30.79                             | 3.8861             | 1.878      | 1.986                   | 2.103                   |
|      | c                | –30.81                             | 3.8858             | 1.942      | 2.021                   | 2.021                   |
| 0.50 | d                | –28.94                             | 3.8921             | 1.944      | 1.945                   | 2.035                   |
|      | e                | –28.94                             | 3.8935             | 1.863      | 1.917                   | 2.030                   |
|      | f                | –28.93                             | 3.8932             | 1.947      | 1.922                   | 2.023                   |
|      | g                | –29.01                             | 3.9065             | 1.890      | 2.022                   | 2.031                   |
|      | h                | –28.92                             | 3.8942             | 1.940      | 1.929                   | 2.036                   |
|      | i                | –28.91                             | 3.8891             | 1.880      | 2.009                   | 2.008                   |

formations as we will see later. Literature usually reference the charge of the atoms that we use in this work as  $\text{Ba}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Fe}^{+3/+4}$ ,  $\text{Cu}^{+2/+3}$  and  $\text{O}^{-2}$ . Here we employ the Bader charge analysis to calculate the effective charge of the atoms (results are showed in Table 2). In the case of Ba/Sr the calculated effective charge is 1.57e for Ba and 1.60e for Sr, which is approximately the ionic charges and demonstrated to be almost independent of the iron content. However the charges of the Fe, Cu and O atoms are far away of the

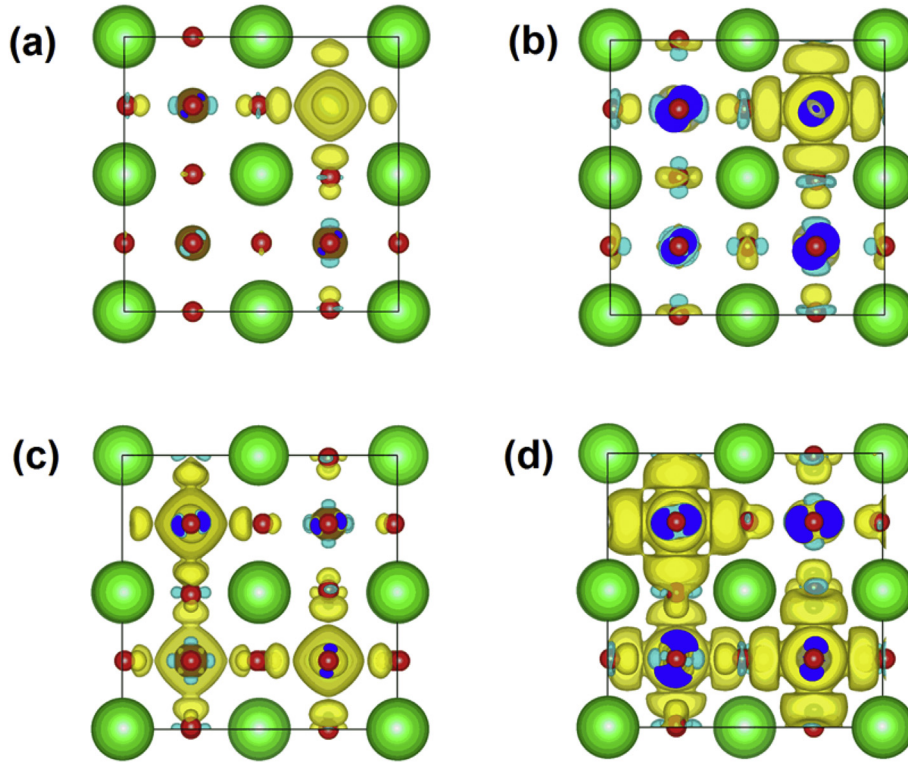
ionic charges and this indicates a strong covalence of the B–O chemical bond. The effective charge for Fe ( $\sim 1.83\text{e}$ ) it is almost independent of the Cu-doping. The copper in the compositions  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.75}\text{Cu}_{0.25}\text{O}_3$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Cu}_{0.5}\text{O}_3$  has a charge of 1.20e and 1.29e respectively which is near the formal state  $\text{Cu}^{+2}$  that induces the Jahn Teller effect. The magnetic moments for the B-site atoms listed in Table 2 are  $\approx 3.2 \mu_B$  for Fe and  $0.46 \mu_B$  for Cu which are in accordance with the calculated charges. The charge difference of Cu-containing perovskites and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$  is shown in Fig. 2. This clearly shows the electron density excess of Cu is bounded to the oxygen neighbors.

**Table 2**  
Results of Bader charge analysis for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Cu}_x\text{O}_3$  and magnetization of B-site atoms.

| x    | Ba     | Sr     | Fe     | Cu     | O      | $\mu_{\text{Fe}}/\mu_B$ | $\mu_{\text{Cu}}/\mu_B$ |
|------|--------|--------|--------|--------|--------|-------------------------|-------------------------|
| 0    | +1.56e | +1.60e | +1.84e | –      | –1.14e | 3.62                    | –                       |
| 0.25 | +1.57e | +1.60e | +1.83e | +1.20e | –1.08e | 3.20                    | 0.46                    |
| 0.50 | +1.57e | +1.60e | +1.83e | +1.29e | –1.04e | 3.01                    | 0.46                    |

### 3.2. Temperature influence in the cathode stability

Cathodes under SOFCs conditions must be designed to support temperatures in the 500–700 °C range for the intermediate



**Fig. 2.** Charge density difference of Cu-doped perovskites and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$  showing where is located the electron density excess of Cu. The isosurfaces are plotted for  $x = 0.25$  at (a)  $-0.006$  and (b)  $-0.002$  and for  $x = 0.50$  at (c)  $-0.006$  and (d)  $-0.002$   $\text{e}/\text{\AA}^3$  with VESTA [53].

temperature SOFCs and 800–1000 °C range for high temperature SOFCs. Perovskites based on  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$  are promising for SOFCs due to its high thermodynamic stability. To calculate the relative stability of the compounds we evaluate the Gibbs free energy change for the decomposition of the  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Cu}_x\text{O}_3$  perovskites into BaO, SrO, CuO and  $\text{Fe}_2\text{O}_3$  as the most stable oxides and the O<sub>2</sub> molecule. The Gibbs free energy for the solids it is described as [15]:

$$G_{\text{solid}} = E_{\text{solid}} + G_{\text{vib}} - TS_{\text{solid}} + PV_{\text{solid}} \quad (1)$$

where the  $E_{\text{solid}}$  is the total energy from 0K DFT calculation corresponding to the electronic structure,  $G_{\text{vib}}$  is the Gibbs free energy from vibrations,  $T$  is the temperature,  $S_{\text{solid}}$  is the configurational entropy,  $P$  in the external pressure,  $V_{\text{solid}}$  in the solid volume. As approximation, we neglect the  $TS_{\text{solid}}$  term due it is a much lower than the vibrational part at temperatures far from the 0 K and also the  $PV_{\text{solid}}$  term because has a small contribution for the working pressures of the SOFCs ( $\sim 1$  atm). The Gibbs free energy for the decomposition of ABO<sub>3</sub> was calculated according to:

$$\Delta G_{\text{dec}} = G_{\text{AO}} + \frac{1}{x} G_{\text{B}_x\text{O}_y} + \left(2 - \frac{y}{x}\right) \mu_{\text{O}} - G_{\text{ABO}_3} \quad (2)$$

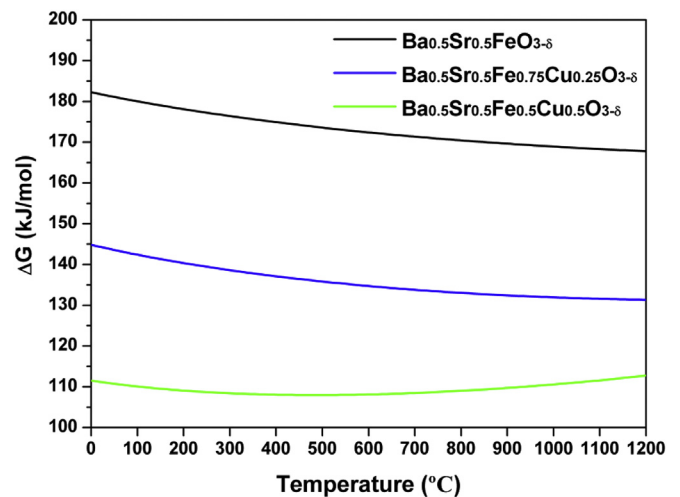
where the  $G_{\text{AO}}$  is the free energy from the A-site cation in their most stable oxide form,  $G_{\text{B}_x\text{O}_y}$  is the free energy from the B-site cation in their most stable oxide form,  $\mu_{\text{O}}$  is the free energy of oxygen (normalized per O) and  $G_{\text{ABO}_3}$  is the free energy of the ABO<sub>3</sub> perovskite. The  $\mu_{\text{O}}$  can be derived from:

$$\mu_{\text{O}}(T) = \frac{1}{2} \left[ E_{\text{O}_2}^{\text{VASP}} + \Delta h_{\text{O}_2}^0 \right] + \Delta \mu_{\text{O}}^0(T) \quad (3)$$

where  $E_{\text{O}_2}$  is the O<sub>2</sub> energy in their triplet state calculated with VASP at  $T = 0$  K,  $\Delta h_{\text{O}_2}^0$  is the 1.36 eV correction suggested by Wang

et al. [42] to correct the GGA binding energy and  $\Delta \mu_{\text{O}}^0(T)$  is a polynomial fitting of experimental data [43].

The  $\Delta G_{\text{dec}}(T)$  energies for different compositions are showed in Fig. 3. In all the cases the evaluated decomposition of the perovskites is not favorable in the temperature range from 0 to 1200 °C. However, if we compare the structures between them, it is clearly that the most stable structure it is  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$  and the inclusion of Cu to the  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$  structure becomes this more unstable. For  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.75}\text{Cu}_{0.25}\text{O}_{3-\delta}$  the  $\Delta G_{\text{dec}}(T)$  decays monotonically with temperature, however for the case of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Cu}_{0.5}\text{O}_{3-\delta}$  the decomposition becomes to be more



**Fig. 3.** Gibbs free energy for perovskite decomposition in their most stable oxides calculated at  $P = 0$  atm. The corresponding reactions are listed in Table 3.

favorable with the increase of temperature until 750 °C where reaches a minimum and after that point the  $\Delta G_{\text{dec}}(T)$  slowly increase. Table 3 shows a summary of the  $\Delta G_{\text{dec}}(T)$  evaluated at different temperatures to compare their stability. This first approach to evaluate the perovskite stability only considers the Cu-doping, but the inclusion of oxygen non-stoichiometry also affects the perovskite stability which is beyond the objective of this work.

### 3.3.. Oxygen vacancy formation

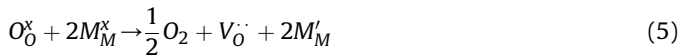
Evaluate the oxygen vacancy formation it is important for development of MIECs because the creation of oxygen point defects it is necessarily for bulk diffusion and oxygen incorporation according to [13]:



where in Kröger-Vink notation,  $\text{V}_\text{O}^{\cdot\cdot}$  represents an oxygen vacancy with two effective charges,  $\text{O}_\text{O}^\times$  represents a neutral oxygen ion in an oxygen site, and  $h^\cdot$  denotes a positively charged electron hole.

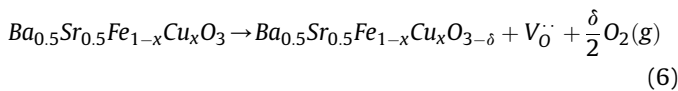
The cobalt-based perovskites with composition  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$  and specially the composition  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  combines a high mobility of the oxygen vacancies and a high degree of vacancies. A previous work performed by Kotomin et al. [44] using the functional GGA-PBE, calculated the oxygen vacancy formation energies,  $E_{\text{vac}}$ , for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$  perovskites. Their results show that the  $E_{\text{vac}}$  increases with the Fe content almost linearly from 1.2 eV ( $x = 0$ ) to 2.2 eV ( $x = 1$ ). These values allow to explain the effect of iron inclusion but they overestimate the experimental oxidation enthalpies ( $\Delta H_{\text{ox}} = -E_{\text{vac}}$ ) for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$  perovskites ( $-47 \text{ kJ mol}^{-1}$  for  $x = 0.2$  at  $\delta = 0.52$  and  $-58 \text{ kJ mol}^{-1}$  for  $x = 1$  at  $\delta = 0.34$  [45]).

In contrast to the B-site cation arrangement, the vacancies formation energies strongly depend of the nearest neighbors because the vacancy formation reaction involves charge redistribution according to:



where in Kröger-Vink notation,  $M_\text{M}^\times$  is a B-site metal ( $M = \text{Fe}, \text{Cu}$  or both) with their initial formal charge,  $M_\text{M}'$  is the B-site metal with an extra electron.

The vacancy formation energy was calculated using the oxygen molecule in the triplet state as final product according to the reaction:



The  $E_{\text{vac}}$  was calculated using all the possible B-site environments ( $\text{Fe}-\text{V}_\text{O}^{\cdot\cdot}-\text{Fe}$ ,  $\text{Fe}-\text{V}_\text{O}^{\cdot\cdot}-\text{Cu}$  and  $\text{Cu}-\text{V}_\text{O}^{\cdot\cdot}-\text{Cu}$ ) according to the equation:

$$E_{\text{vac}} = \left( E_{\text{ABO}_{3-\delta}(\text{s})} + \frac{\delta}{2} E_{\text{O}_2(\text{g})} \right) - E_{\text{ABO}_3(\text{s})} \quad (7)$$

**Table 3**  
Gibbs free energy for perovskite decomposition.

|                                                                                                                                                                                  | $\Delta G_{\text{dec}}$ (kJ/mol) |            |             |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------|------------|-------------|
|                                                                                                                                                                                  | T = 25 °C                        | T = 700 °C | T = 1200 °C |
| $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3 \rightarrow 1/2\text{BaO} + 1/2\text{SrO} + 1/2\text{Fe}_2\text{O}_3 + 1/4\text{O}_2$                                                | 181.6                            | 171.3      | 169.4       |
| $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.75}\text{Cu}_{0.25}\text{O}_3 \rightarrow 1/2\text{BaO} + 1/2\text{SrO} + 3/8\text{Fe}_2\text{O}_3 + 1/4\text{CuO} + 5/16\text{O}_2$ | 144.1                            | 133.8      | 132.3       |
| $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.50}\text{Cu}_{0.50}\text{O}_3 \rightarrow 1/2\text{BaO} + 1/2\text{SrO} + 1/4\text{Fe}_2\text{O}_3 + 1/2\text{CuO} + 3/8\text{O}_2$  | 111.1                            | 108.5      | 109.9       |

The results of  $E_{\text{vac}}$  calculations are listed in Table 4, taking one point defect/supercell ( $\delta = 0.125$ ) and two point defect/supercell ( $\delta = 0.250$ ). As a general trend the  $E_{\text{vac}}$  decreases with the inclusion of Cu in the structure (Fig. 4). For each composition, the energies strongly depend of the local B-site environment and also of the defect content denoted by  $\delta$ . The  $E_{\text{vac}}$  increases in all the environments when  $\delta$  changes from 0.125 to 0.250 which indicates that the oxidation enthalpy becomes more exothermic to reach a high level of vacancies.

The compound  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  have  $E_{\text{vac}}$  of 1.807 eV for  $\delta = 0.125$  and 2.290 eV for  $\delta = 0.250$  overestimates the oxidation enthalpy for this compound. In the case of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.75}\text{Cu}_{0.25}\text{O}_{3-\delta}$  the vacancies are more favorable to stay in the  $\text{Fe}-\text{V}_\text{O}^{\cdot\cdot}-\text{Cu}$  environment (lower  $E_{\text{vac}}$ ). The Cu-doping of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  perovskite affects the local environment of the Cu and also decreases the  $E_{\text{vac}}$  of all the environments. In the case of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Cu}_{0.5}\text{O}_{3-\delta}$  the same trend is repeated, the Cu-doping facilitate the vacancy formation and the  $E_{\text{vac}}$  is much easily formed than previous compositions (specially for  $\text{Fe}-\text{V}_\text{O}^{\cdot\cdot}-\text{Cu}$  and  $\text{Cu}-\text{V}_\text{O}^{\cdot\cdot}-\text{Cu}$ ). Here due to the B-site arrangement it is possible to accommodate a vacancy between two coppers ( $\text{Cu}-\text{V}_\text{O}^{\cdot\cdot}-\text{Cu}$ ) and compared to other environments, this is the most probable place to locate an oxygen vacancy. As a general trend the  $E_{\text{vac}}$  augment according to the series  $\text{Cu}-\text{V}_\text{O}^{\cdot\cdot}-\text{Cu} < \text{Fe}-\text{V}_\text{O}^{\cdot\cdot}-\text{Cu} < \text{Fe}-\text{V}_\text{O}^{\cdot\cdot}-\text{Fe}$  and also with the increase of vacancy content  $\delta$ .

The oxygen loss from the structure implies a change in the electronic structure. The removal of a neutral oxygen atom leads to a charge redistribution (two electrons from the oxygen atom) which mostly are located in the nearest B-cations [13]. Table 4 shows the oxygen vacancy local environment and the charge difference associated with the creation of a point defect calculated using Bader charge analysis. The calculations show an electron charge redistribution that prefers Cu over Fe as a target for the additional electrons. So the lower  $E_{\text{vac}}$  is related with the electron acceptor character of Cu compared to Fe.

### 3.4.. Oxygen bulk diffusion

Here we study the oxygen migration barriers to understand the effect of Cu-doping. For perovskites with the simple formula  $\text{ABO}_{3-\delta}$ , the oxygen path oxygen migration is a jump of the oxygen atom into a vacancy  $\text{V}_\text{O}^{\cdot\cdot}$  along the edge of a deficient  $\text{BO}_6$  octahedron (actually a re-orientation of the apex of a  $\text{BO}_5$  pyramid). During the transition state the oxygen ion passes through a triangle formed by the an B-cation and two A-cation [44] as can be seen in Fig. 5.

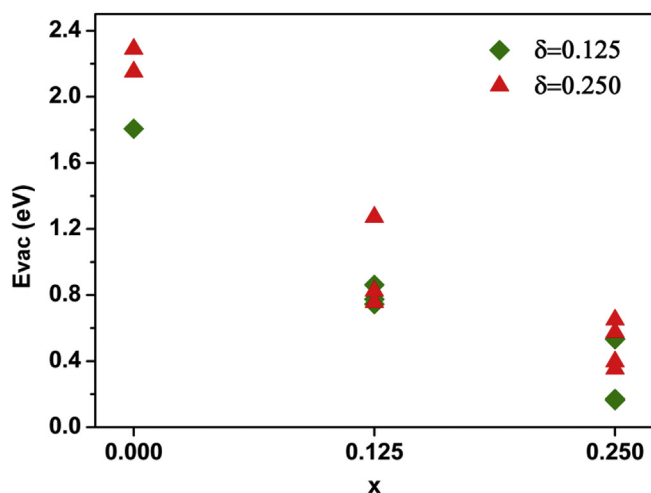
We performed calculations for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  perovskites considering the effect of the vacancy levels. The results are summarized in Table 5 showing vacancy content, initial and final local environment, transition state configuration, migration-energy barriers and activation barriers.

The composition  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  has a migration barrier 0.590 eV and 0.759 eV for  $\delta = 0.125$  and  $\delta = 0.250$  respectively. This energy is very close to the  $E_m$  of 0.72 eV reported by Kotomin et al. [44] for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  for  $\delta = 0.125$ . However, as can be expected, the energy for vacancy hopping increases with the  $\delta$  content. For the compound  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.75}\text{Cu}_{0.25}\text{O}_{3-\delta}$  we have an unexpected

**Table 4**

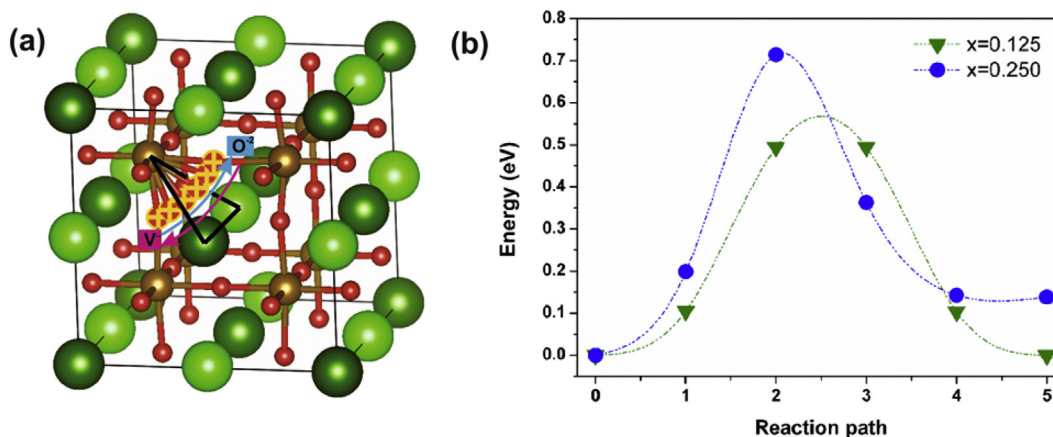
Oxygen vacancy formation energies and charge difference in the nearest B cations.

| x    | $\delta = 0.125$      | $E_{vac,1}$ (eV) | $\Delta q_1$ | $\Delta q_2$ | Cell parameter (Å) | $\delta = 0.250$      | $E_{vac,2}$ (eV) | $\Delta q_1$ | $\Delta q_2$ | Cell parameter (Å) |
|------|-----------------------|------------------|--------------|--------------|--------------------|-----------------------|------------------|--------------|--------------|--------------------|
| 0    | Fe–V <sub>O</sub> –Fe | 1.807            | –0.09e       | –0.09e       | 3.8978             | Fe–V <sub>O</sub> –Fe | 2.290            | –0.08e       | –0.08e       | 3.9007             |
| 0.25 | Fe–V <sub>O</sub> –Fe | 0.862            | –0.08e       | –0.08e       | 3.9005             | Fe–V <sub>O</sub> –Fe | 1.273            | –0.08e       | –0.08e       | 3.9033             |
|      | Fe–V <sub>O</sub> –Cu | 0.745            | –0.09e       | –0.11e       | 3.8923             | Fe–V <sub>O</sub> –Cu | 0.825            | –0.09e       | –0.11e       | 3.9038             |
| 0.50 | Fe–V <sub>O</sub> –Fe | 0.533            | –0.08e       | –0.08e       | 3.9049             | Fe–V <sub>O</sub> –Fe | 0.734            | –0.08e       | –0.08e       | 3.9054             |
|      | Fe–V <sub>O</sub> –Cu | 0.164            | –0.08e       | –0.11e       | 3.9051             | Fe–V <sub>O</sub> –Cu | 0.397            | –0.08e       | –0.10e       | 3.9160             |
|      | Cu–V <sub>O</sub> –Cu | 0.110            | –0.11e       | –0.11e       | 3.9050             | Cu–V <sub>O</sub> –Cu | 0.354            | –0.12e       | –0.12e       | 3.9348             |

**Fig. 4.** Oxygen vacancy energy formation ( $E_{vac}$ ) for  $Ba_{0.5}Sr_{0.5}Fe_{1-x}Cu_xO_{3-\delta}$ .

behaviour in the migration barrier. Some configurations have a  $E_{mig}$  superior that  $Ba_{0.5}Sr_{0.5}FeO_{3-\delta}$  and in other cases is lower. Nevertheless, if we see the transition state configurations, the energy for migration in the triangle  $\Delta(Ba-Fe-Sr)$  are 0.544 eV ( $\delta = 0.125$ ) and 0.802 eV ( $\delta = 0.250$ ) and for the triangle  $\Delta(Ba-Cu-Sr)$  are 1.081 eV ( $\delta = 0.125$ ) and 1.004 eV ( $\delta = 0.250$ ). So the transition state plays a preponderant role in the behaviour of oxygen diffusion. We saw the Cu-doping decreases  $E_{vac}$  due the Cu accepted more easily the electrons from charge redistribution after the vacancy formation, however if we consider the oxygen intermediate state it is more probable that the migration path is along the edge of a  $FeO_6$  octahedron.

In the case of the  $Ba_{0.5}Sr_{0.5}Fe_{0.5}Cu_{0.5}O_{3-\delta}$  the transition state has the same behaviour; the migration path along the edge of a  $FeO_6$  has a lower  $E_{mig}$  than  $CuO_6$ . This compound shows, for the transition state configuration  $\Delta(Ba-Fe-Sr)$ , an energy of 0.465 eV ( $\delta = 0.125$ ) and 0.197 eV ( $\delta = 0.250$ ) and for  $\Delta(Ba-Cu-Sr)$  energies of 0.946 eV ( $\delta = 0.125$ ) and 0.832 eV ( $\delta = 0.250$ ). However if we focus on the transition state  $\Delta(Ba-Cu-Sr)$  for  $Ba_{0.5}Sr_{0.5}Fe_{0.75}Cu_{0.25}O_{3-\delta}$  and  $Ba_{0.5}Sr_{0.5}Fe_{0.5}Cu_{0.5}O_{3-\delta}$ , there is a particular behaviour, for these

**Fig. 5.** (a) Oxygen/vacancy migration mechanism and (b) energy migration barrier  $Ba_{0.5}Sr_{0.5}FeO_{3-\delta}$  with  $\delta = 0.125$  and  $\delta = 0.250$ .**Table 5**Oxygen migration barriers with initial, final and transition states for  $Ba_{0.5}Sr_{0.5}Fe_{1-x}Cu_xO_{3-\delta}$ .

|          | Vacancy content  | Initial position      | Final position        | Transition state   | $E_{vac}$ (eV) | $E_{mig}$ (eV) | $E_{act}$ (eV) |
|----------|------------------|-----------------------|-----------------------|--------------------|----------------|----------------|----------------|
| x = 0    | $\delta = 0.125$ | Fe–V <sub>O</sub> –Fe | Fe–V <sub>O</sub> –Fe | $\Delta(Ba-Fe-Sr)$ | 1.807          | 0.590          | 2.397          |
|          | $\delta = 0.250$ | Fe–V <sub>O</sub> –Fe | Fe–V <sub>O</sub> –Fe | $\Delta(Ba-Fe-Sr)$ | 2.290          | 0.759          | 3.049          |
| x = 0.25 | $\delta = 0.125$ | Fe–V <sub>O</sub> –Fe | Fe–V <sub>O</sub> –Cu | $\Delta(Ba-Fe-Sr)$ | 0.862          | 0.544          | 1.405          |
|          |                  | Fe–V <sub>O</sub> –Cu | Fe–V <sub>O</sub> –Cu | $\Delta(Ba-Cu-Sr)$ | 0.745          | 1.081          | 1.826          |
|          | $\delta = 0.250$ | Fe–V <sub>O</sub> –Fe | Fe–V <sub>O</sub> –Cu | $\Delta(Ba-Fe-Sr)$ | 1.273          | 0.802          | 2.074          |
|          |                  | Fe–V <sub>O</sub> –Cu | Fe–V <sub>O</sub> –Cu | $\Delta(Ba-Cu-Sr)$ | 0.825          | 1.004          | 1.828          |
| x = 0.50 | $\delta = 0.125$ | Fe–V <sub>O</sub> –Fe | Fe–V <sub>O</sub> –Cu | $\Delta(Ba-Fe-Sr)$ | 0.533          | 0.465          | 0.998          |
|          |                  | Fe–V <sub>O</sub> –Cu | Fe–V <sub>O</sub> –Cu | $\Delta(Ba-Cu-Sr)$ | 0.534          | 0.946          | 1.480          |
|          | $\delta = 0.250$ | Fe–V <sub>O</sub> –Cu | Fe–V <sub>O</sub> –Cu | $\Delta(Ba-Fe-Sr)$ | 0.651          | 0.197          | 0.848          |
|          |                  | Fe–V <sub>O</sub> –Cu | Cu–V <sub>O</sub> –Cu | $\Delta(Ba-Cu-Sr)$ | 0.575          | 0.832          | 1.407          |

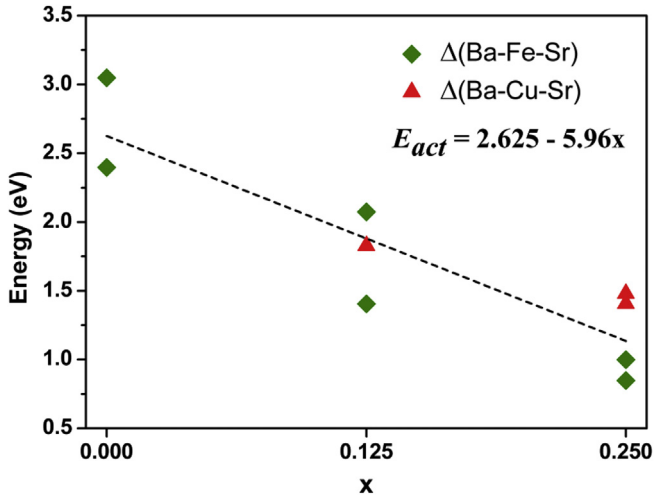


Fig. 6. Diffusion activation barrier ( $E_{act}$ ) for the series  $Ba_{0.5}Sr_{0.5}Fe_{1-x}Cu_xO_{3-\delta}$ .

transitions the  $E_{mig}$  decreases when the vacancy concentration is higher.

The diffusion activation energy can be predicted using the oxygen vacancy formation energy ( $E_{vac}$ ) and the oxygen migration energy ( $E_{mig}$ ) according to [46]:

$$E_{act} = E_{mig} + E_{vac} \quad (8)$$

The results of  $E_{act}$  (see Table 5) demonstrate that the Cu-doping clearly reduces the activation barrier energies for oxygen diffusion (see Fig. 6).

### 3.5. Electronic structure

The concepts of vacancy formation energies and oxygen diffusion are important to predict the ORR activity. Furthermore, to have a complete understanding of this phenomena it is necessary to model surfaces using slabs to calculate adsorption or chemisorption energies [46,47] and calculate reaction mechanisms [14,48,49]. Lee et al. [50] have proposed a novel view based on catalysis experience, which uses a first-principles descriptor for designing ORR

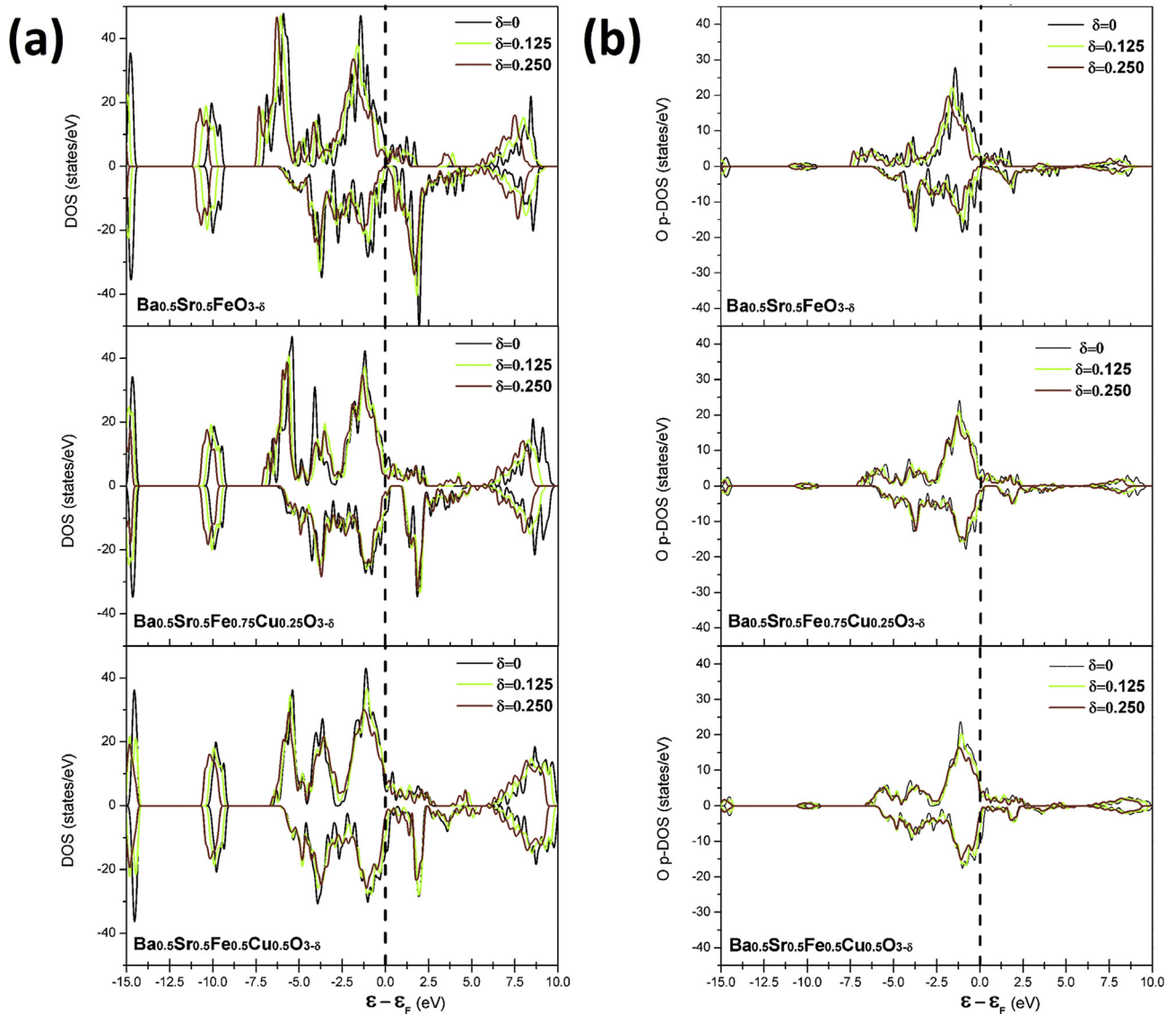


Fig. 7. (a) Electronic density of states (DOS) and (b) oxygen p-band density of states (O p-DOS) taking as reference the fermi level ( $\epsilon_F$ ).

**Table 6**  
Oxygen p-band centre respect to fermi level ( $\epsilon_F$ ).

| $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$ | $\delta = 0$ | $\delta = 0.125$ | $\delta = 0.250$ |
|-------------------------------------------------------------------------------|--------------|------------------|------------------|
| $x = 0$                                                                       | −1.42        | −1.66            | −1.94            |
| $x = 25$                                                                      | −1.26        | −1.32            | −1.49            |
| $x = 50$                                                                      | −1.12        | −1.14            | −1.31            |

catalyst. They proposed a descriptor based in electronic structure consisting in the relative position of the oxygen p-band centre in reference to the Fermi level ( $\epsilon_F$ ). They show a correlation between the O-p band centre and vacancy formation energies ( $E_{\text{vac}}$ ), oxygen surface exchange coefficient ( $k^*$ ) and area specific resistance (ASR).

We calculate the density of states (DOS) and the projected-density of states (p-DOS) for O-p band, as can be seen in Fig. 7. The DOS shows, for all the compositions, a metallic character which is different from the semiconductor behaviour from conductivity vs temperature measurements [51,52]. However if we compare the DOS for the  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$ , near the Fermi level for the same vacancy content  $\delta$ , there are more available states as the Cu-doping increases and this enhance the electric conduction as experimental results indicates [51].

The centroids of the p-band expressed in reference to  $\epsilon_F$  are shown in Table 6. The results indicate that the Cu-free perovskite is the less active ORR catalyst of the series and the activity is promoted by the Cu-doping. Additionally, if we compare the effect of  $\delta$ , the introduction of oxygen defects to the structure shifts the p-band centre away from the fermi level giving a reduction in the ORR activity.

#### 4.. Conclusion

In summary, we have described the key bulk properties of the perovskites  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  in order to understand the high catalytic activity for ORR obtained in previous work [23]. The Cu-doping reduces the oxygen vacancy formation energies for all the local environments ( $\text{Fe}-\text{V}_\text{O}^\bullet-\text{Fe}$ ,  $\text{Fe}-\text{V}_\text{O}^\bullet-\text{Cu}$  and  $\text{Cu}-\text{V}_\text{O}^\bullet-\text{Cu}$ ) preferring a location near the Cu sites. The charge density is higher in the surrounding of copper compared with iron, and the formation of point defects generates a charge redistribution, in which the Cu accepts more easily the electrons (lower formal charge) when compared with Fe.

The study of oxygen bulk diffusion also demonstrates the activation barrier can be decreased with the Cu-doping. Nevertheless, the most probable path for oxygen migration is along the edge of a  $\text{FeO}_6$  octahedron and not in the  $\text{CuO}_6$  octahedron. This fact could be attributed to the highest electron density of Cu, which implies the passage of the oxygen trough the transition state  $\Delta(\text{Ba}-\text{Cu}-\text{Sr})$  with a higher electron density.

The oxygen reduction reaction (ORR) activity estimation approach was adopted using as descriptor the energy difference between the bulk O p-band centre and the Fermi level. The Cu-doping brings the O p-band closer to the Fermi level and promotes the ORR activity.

Along this work we aim to understand the improvement of the ORR activity using bulk properties of the perovskites  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  which allows understanding the experimental results obtained in previous work. To get a deeper comprehension of the ORR it is necessarily to use perovskite surfaces to model the oxygen reduction reaction process which is the aim of our future work.

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