



Simulations of REBaCo₂O_{5.5} (RE=Gd, La, Y) cathode materials through energy minimisation and molecular dynamics

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ABSTRACT

The GdBaCo₂O_{5+x} oxide has been presented as a promising cathode material for solid oxide fuel cells. It presents very high oxygen exchange and diffusion coefficients, two characteristics of utmost importance for an efficient cathode material. Yet the understanding at atomic scale of these two properties is rather limited. Here, we performed calculations to understand the influence of rare-earth nature in REBaCo₂O_{5.5} (RE=Gd, La, Y) on material stability and oxygen diffusion properties. Through energy minimisation, we determined the most energetically favourable distribution of A-site cations and oxygen vacancies. We also investigated with Molecular Dynamics simulations the mechanisms of oxygen diffusion in A-site ordered REBaCo₂O_{5.5}. The results confirm that oxygen vacancies essentially lie in the RE-plane and that diffusion is mainly two-dimensional with oxygen moving in the (a,b) plane while diffusion along the c axis is strongly hindered. Between 1300 and 1900 K, the activation energy for oxygen diffusion lies in the range 0.69–0.83 eV depending on the RE cation nature, values in good agreement with the experimental ones. We show that, in the double perovskite structure, the replacement of Gd by a larger rare-earth ion enhances oxygen diffusion properties but also reduces the stability of the double perovskite structure.

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1. Introduction

Solid Oxide Fuel Cells (SOFCs) are electrochemical devices that allow converting hydrogen and air into electricity and heat. These systems are known to work at high temperature, which represents some advantages from the point of view of fuel tolerance and efficiency but also some significant drawbacks due to an accelerated ageing of components. The great majority of research works in the field aim thus at lowering the working temperature around 750–800 °C or even lower to ensure a very low degradation of cell components in working conditions. At these temperatures, not only the losses due to the electrolyte but also to electrode reactions start to be limiting [1,2]. Then, the lowering of working temperature supposes to find new electrode materials with enhanced electrochemical properties. For finding new electrolyte and electrode materials, not only empirical approaches but also theoretical predictions [3] have been used providing in the latter case a correlation between macroscopic performance and atoms behaviour at the atomistic scale.

Recently, the double perovskite cobaltite compound, GdBaCo₂O_{5+x} (GBCO), has been proposed as a promising cathode material for SOFCs [4,5]. Several studies have been performed to understand the diffusion properties of oxygen at atomic scale in this material. In particular, we determined by Molecular Dynamics (MD) simulations that oxygen

diffusion has a strong anisotropic nature in GBCO, occurring essentially in the (a,b) plane [6]. We also showed that the oxygen diffusion mechanism was driven by the presence of vacancies in both the rare-earth and the cobalt planes. Indeed, 95% of oxygen vacancies were found to lie in the Gd plane, the remaining 5% being located in the cobalt plane. The Barium plane was shown to act as a barrier for oxygen diffusion. This result was confirmed by Chroneos et al. [7] who also proved that the ordering of Gd and Ba along the c-axis allows for a better oxygen diffusion compared to the fully disordered situation.

In this work, we extend the previous study realized on GBCO to compounds with other trivalent cations i.e. La and Y. These compounds will be named LBCO and YBCO. These cations present different ionic radii, being 1.053 Å, 1.16 Å and 1.019 Å in 8-fold environment for Gd, La and Y respectively. By performing energy minimization calculations, we first identified the preferential RE/Ba configuration for cations on the A-site and the preferential site for oxygen vacancies. Afterwards, MD simulations were performed to identify how the nature of the RE ion affects the transport properties.

1.1. Calculation details

Energy minimization and MD calculations were performed, both applied to compounds with chemical formula REBaCo₂O_{5.5} (RE = Gd, La, Y) i.e. to a material with a fixed oxygen content. For practical reasons, the oxygen stoichiometry has been fixed at 5.5 (per formula unit). This allows to put a formal charge of +3 on cobalt atoms. This composition is very close to the one observed between room temperature and

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roughly 400 °C. Above 400 °C in air, these compounds usually release oxygen at a faster rate as temperature increases. Thus our system with constant stoichiometry will permit to obtain reliable information about the diffusion mechanisms but may present intrinsic errors in reproducing the experimental evolution of diffusion coefficient with temperature, as obtained from tracer or relaxation measurements.

An energy minimization approach was employed to determine the energies of configurations having different cation distributions on the A-site and different distributions of oxygen atoms. These calculations were done using the GULP code [8], working on 3*3*4 perovskite supercells i.e. containing 18 chemical formulas. Five different cases were considered corresponding to different atomic distributions. For each case, 10 different configurations were analyzed to get a better statistical description.

- Case 1: Random distribution of RE (RE=G, La, Y) and Ba cations on A-site. Random distribution of oxygen vacancies
- Case 2: Ordering along the c-axis of RE and Ba cations. Random distribution of oxygen vacancies
- Case 3: Ordering along the c-axis of RE and Ba cations. Oxygen vacancies randomly located in the Ba-plane
- Case 4: Ordering along the c-axis of RE and Ba cations. Oxygen vacancies randomly located in the Co-plane
- Case 5: Ordering along the c-axis of RE and Ba cations. Oxygen vacancies randomly located in the RE-plane

The distribution of atoms giving the smallest energy (i.e. the most stable) was then chosen to build the box for MD calculations. MD simulations were done with the DLPOLY Classic code [9,10] using a supercell of 8×8×8 cubic perovskite unit cells (containing 256 Ba, 256 RE, 512 Co and 1408 O atoms and 128 oxygen vacancies), also corresponding to the general chemical formula REBaCo₂O_{5.5}. As described below, the distribution chosen was that of a cation ordering on A-site along the c-axis and the presence of vacancies in the RE-plane (case 5). Practically, during these simulations, the system was first equilibrated at several temperatures between 1300 and 1900 K and at zero pressure for 20,000 time steps (with a time step of 0.5 fs) in the isothermal-isobaric (NPT) ensemble with the Nosé-Hoover thermostat. Afterwards, the equilibrium lattice parameters were calculated with 100,000 time steps more. Then, simulations were performed in the NVT mode during 100,000 time steps, after a 10,000 equilibration steps. Finally, NVE simulations were realized corresponding to 1,000,000 to 2,000,000 time steps. Let us clarify that an orthorhombic structure was generally obtained after the NPT step but if a tetragonal structure was imposed for the NVT and NVE steps, having the same volume than the orthorhombic one, the final diffusion coefficients (deduced from the NVE simulations) of the tetragonal and orthorhombic structures were very close to each other (the difference is less than 5% whatever the temperature).

Either for energy minimization or for molecular dynamics simulations, interactions between ions were described by a long-range Coulombic term calculated by Ewald summation and a short-range Buckingham pair potential. For Coulombic interactions, the formal charges +2, +3, +3 and −2 were used respectively for Ba, RE, Co and O ions. The use of formal ionic charge was shown to describe correctly the dynamical features of atoms in most oxide compounds. The Buckingham potential is described by:

$$\varphi_{ij}(r) = A_{ij} \exp\left(-\frac{r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6} \quad (1)$$

where r is the distance between the atoms i and j , and A_{ij} , ρ_{ij} and C_{ij} are potential parameters specific to each ion pair whose values are given in Table 1. The set of potentials was taken from previous studies, which were shown to reproduce correctly oxide materials properties [11–13].

Table 1

Inter-atomic Buckingham potentials used for energy minimisation and molecular dynamics calculations. M–O interactions are taken from: Gd–O [6], La–O and Y–O [12,13], Co–O [11].

Interaction	A (eV)	ρ (Å)	C (eV.Å ⁶)
Gd ³⁺ –O ^{2−}	1458.38	0.3522	0.0
La ³⁺ –O ^{2−}	1545.21	0.3590	0.0
Y ³⁺ –O ^{2−}	1310.00	0.3561	0.0
Ba ²⁺ –O ^{2−}	1214.4	0.3537	0.0
Co ³⁺ –O ^{2−}	1329.82	0.3087	0.0
O ^{2−} –O ^{2−}	22764.3	0.149	43.0

2. Results and discussion

The results of energy minimization are shown in Fig. 1. In this figure, only the relative energy between the different configurations is plotted in order to put all compositions on a same graph. For a same composition, the reference energy has been arbitrarily chosen to be the energy of case 1. This figure clearly shows that, as a general rule, the A-site cation ordered material is more stable than the fully disordered one (case 1). These calculations also indicate that strong differences in energy exist depending on oxygen vacancies location. In all cases, configurations where oxygen vacancies are located in the RE plane are always more stable than configurations with vacancies located in the Ba or Co planes. Besides, if we compare the most stable configuration with A-site ordering and oxygen vacancies in the RE plane to the fully random configuration, it seems that the relative stability of the ordered phase tends to decrease as the RE cation size increases. This was partly confirmed by experiments which showed that LaBaCo₂O_{5.5} was much more difficult to prepare compared to GdBaCo₂O_{5+x} for instance. Indeed, single phase double perovskite LaBaCo₂O_{5+x} could only be prepared in a small range of P_{O2} in slightly reducing atmosphere [14], while GBCO could be prepared in air without extra care of the atmosphere. One consequence of this is that the stability of LaBaCo₂O_{5+x} in air atmosphere i.e. in the working conditions of a SOFC cathode, should probably be considered with caution.

In Fig. 2, we present the projection along the a -axis and the c -axis of the mean square displacement of oxygen atoms as a function of time for GBCO, LBCO and YBCO. The presented simulation corresponds to a temperature of 1900 K. This graph shows that oxygen atoms diffuse freely along the a -axis (a very similar curve is obtained for the b -axis) while along the c -axis their displacement is limited. This situation has been already commented previously and was

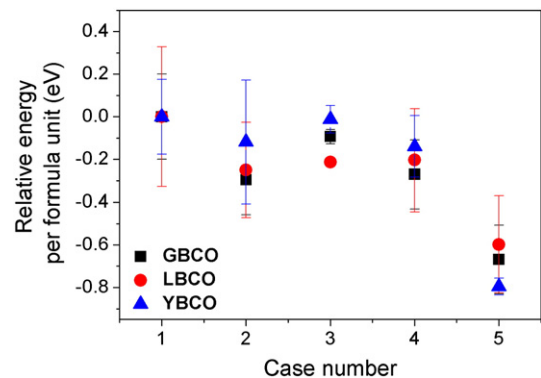


Fig. 1. Relative energy of REBaCo₂O_{5.5} for different cases of cation and oxygen distribution (see text for details) for RE = Gd (black square), RE = La (red circle), RE = Y (blue triangle). The energy of case 1 is taken as a reference.

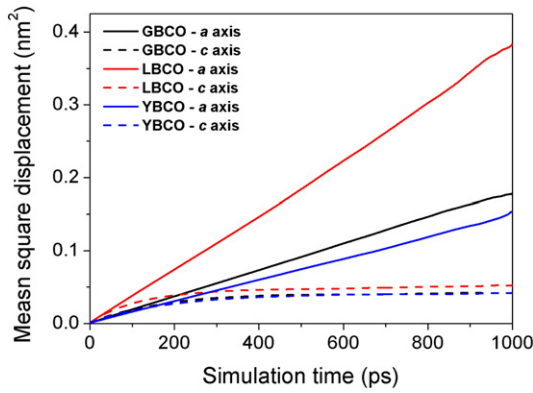


Fig. 2. Projection of oxygen mean square displacement at $T = 1900$ K along the a -axis (straight line) and the c -axis (dashed line) as a function of simulation time for GBCO (black), LBCO (red), YBCO (blue).

associated with the fact that the Ba-planes act as barriers for oxygen diffusion. We show here that this strong anisotropy is reproduced whatever is the RE-cation. This graph also shows that for LBCO, the mean square displacement is larger than for Gd and Y, indicating a probable better diffusion in this compound.

Performing MD simulations, one is also able to extract the oxygen diffusion coefficient from mean square displacement of atoms. These coefficients have been determined here for temperatures between 1300 and 1900 K with a 100 K step. The oxygen diffusion coefficients for GBCO, LBCO, and YBCO are plotted in Fig. 3.

This figure clearly shows that the diffusion coefficient increases according to: $D_O(\text{YBCO}) < D_O(\text{GBCO}) < D_O(\text{LBCO})$. Nevertheless, the difference is still small and diffusion coefficients differ by less than a factor 3. These diffusion coefficients are in reasonable agreement with those determined by other methods such as tracer diffusion or conductivity relaxation. In the latter case, for comparison with our calculations, the deduced chemical diffusion has to be divided by the thermodynamic factor which was calculated to be around 75 in air for temperatures between 1073 and 1273 K [15]. A significant spreading of diffusion coefficient values has nevertheless to be stressed among the published results in literature. In this work, the activation energy for oxygen diffusion is calculated to be $E_a = 0.83$ eV, $E_a = 0.69$ eV, and $E_a = 0.78$ eV for GBCO, LBCO and YBCO respectively, confirming that oxygen transport seems to be favoured in LBCO. The value of activation energy for GBCO is higher than the one determined previously (0.67 eV) but the present values are more reliable due to better statistics and the consideration of

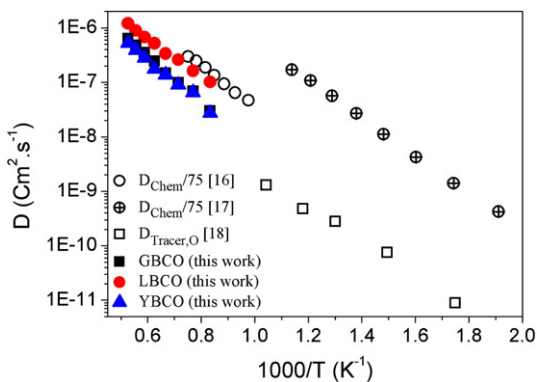


Fig. 3. Calculated diffusion coefficients as a function of the inverse of temperature as extracted from MD simulations for GBCO (black square), LBCO (red circle), YBCO (blue triangle). Comparison with $D_{\text{Tracer,O}}$ and $D_{\text{Chem}}/75$ coefficients for GBCO as taken from [16–18].

more temperatures. The calculated activation energies compare rather well with those reported in GBCO for chemical diffusion coefficients (0.77 eV [16], 0.7 eV [17]) or tracer diffusion coefficients (0.6 eV [18]). They are nevertheless significantly higher than the reported value 0.48 eV reported for $\text{PrBaCo}_2\text{O}_{5+x}$ [19]. In this case, the reported diffusion coefficient was two orders of magnitude higher than any other measurement or prediction. Considering the relative size of the trivalent cation, the evolution of diffusion properties could be explained by the increase of the free volume available for oxygen diffusion. In a way, this behaviour could be related to the effect of tensile strain on ion conducting compounds leading to an enhancement of conduction properties [20]. In order to have a better understanding of the oxygen diffusion mechanisms, we projected the positions of several (7) oxygen atoms along the z direction as a function of time. The result of such projection is shown in Fig. 4. From this figure, one observes that, as mentioned above, oxygen atoms located in the Ba -plane do not escape from this plane. Oxygen atoms located in the RE -plane do not stay in this plane for the whole simulation but rather move to an adjacent Co -Plane. The effective jumps correspond either to a very fast jump from the Co -plane till the same Co -plane through an intermediate position in the RE -plane or to jumps from one Co -plane to the adjacent RE -plane followed by a jump to the other adjacent Co -plane. These effective jumps are at the origin of the high oxygen diffusion coefficient observed in these materials. As mentioned previously, the mere consideration of vacancies in the RE -plane does not enable us to find a percolating path for oxygen atoms. One has thus to consider the presence of vacancies in the Co -plane for a full description of oxygen diffusion mechanism.

We thus calculated the oxygen site occupancy in the Ba -planes, Co -planes and RE -planes by assuming an oxygen atom is in a given plane if its distance to that plane is smaller than half the distance between two adjacent planes. We determined that oxygen site occupancy in the Ba -planes, Co -planes and RE -planes were respectively:

- 99.9%, **97.7%**, 59.3% for GBCO
- 99.8%, **95.3%**, 68.8% for LBCO
- 100.0%, **98.1%**, 57.6% for YBCO

This confirms that most of oxygen vacancies are located in the RE -plane but also that a higher oxygen diffusion-coefficient is correlated to a higher number of oxygen vacancies in the cobalt plane.

3. Conclusion

From energy minimization and molecular dynamics simulations, we have shown that whatever the RE element in $\text{REBaCo}_2\text{O}_{5.5}$, the oxygen diffusion in these double perovskite compounds always occurs in the (a,b) planes while Ba planes act as barrier for oxygen transport. We have shown that oxygen vacancies essentially locate in the RE -plane but that their presence in the Co -plane is mandatory for ensuring high

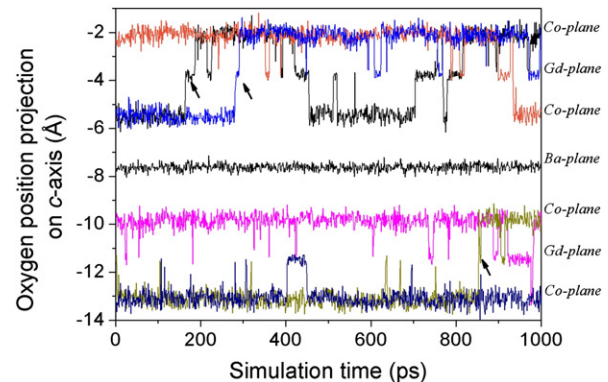


Fig. 4. Projection of the trajectory of eight oxygen atoms along the c -axis as a function of time. Several effective jumps through a RE -plane are indicated with an arrow.

diffusion coefficient. Also, we have shown that the oxygen diffusion coefficient increases as the radius of RE increases. Nevertheless, in this case, the relative stability of the A-site cation ordered phase tends to be smaller, a result that has been confirmed by experiments underlining the difficulty to synthesize $\text{LaBaCo}_2\text{O}_{5+x}$. Larger-size rare-earth cations are more likely to ensure better diffusion properties. However, their reduced stability may limit material applicability.

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