First-principles modeling of $\text{BaCeO}_3$: structure and stabilization of O vacancies by Pd-doping

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We use first-principles density functional theory (DFT) calculations to investigate the ground state structures of both $\text{BaCeO}_3$ (BC) and Pd-doped BC (BCP). The relaxed structures match closely with recent experimental scattering studies, and also provide a local picture of how the BC perovskite lattice accommodates Pd. Both stoichiometric and oxygen-deficient materials are considered, and structures with an O vacancy adjacent to each Pd are predicted to be favored. The oxidation state of Pd in each doped structure is investigated through a structural analysis, the results of which are supported by an orbital-resolved projected density of states. The vacancy stabilization by Pd in BCP is explained through redox chemistry and lattice strain relief.

I. INTRODUCTION

The structure and composition of solid oxide perovskites have been varied widely, in order to tailor their properties for applications \cite{1,2,3,4,5,6,7,8,9}. The development of perovskites as either catalysts themselves or as better oxide supports for catalytic applications is the focus of great current interest. \cite{10,11,12}

Nishihata et al. reported \cite{13,14} that when precious metals (Pt, Rh, or Pd) are mixed into solid oxides of $\text{La(Fe,Co)}_3$, then sintered, the precious metal becomes incorporated within the host perovskite as an oxidized species. When subjected to a reducing atmosphere, the precious metal is extruded from the host matrix and deposited on the surface of the oxide as a fully reduced metal. According to Nishihata et al. this metal is the active species for catalytic reactions, such as the oxidation of CO to CO$_2$. When the reaction is complete, the catalyst is subject to an oxidizing atmosphere. This oxidizes the precious metal, which returns back into the host oxide, where it can be stored for future catalysis. The two-stage cycle can be repeated many times. This increases the efficiency of their catalyst system, presumably because incorporation inhibits precious metal agglomeration under oxidizing conditions. As a result, the catalytic metal retains higher surface area for much longer than on conventional catalytic substrates. This work in so-called “intelligent catalysts” has focused mainly on La-based perovskite hosts, where precious metal dopant levels of up to 5% were achieved.

Based on crystal chemical size rules, we investigated whether the upper limit of 5% precious metal doping is related to the size mismatch between Pd and Fe. For analysis of ionic size in perovskites, the tolerance factor $t$ is the central parameter:

$$t = \frac{R_{A-O}}{R_{B-O} \sqrt{2}}$$

where $R_{A-O}$ is the sum of A and O ionic radii and $R_{B-O}$ is the sum of B and O ionic radii. $\text{LaFeO}_3$ ($r_{\text{La}}=1.36$ Å, $r_{\text{Fe}} \approx 0.6$ Å, $r_{\text{O}}=1.42$ Å) has a tolerance factor of 0.97. The introduction of a Pd$^{+2}$ on the B site ($r_{\text{Pd}}=0.86$ Å) would locally make $t = 0.86$ which would create significant strain and limit solubility. Pd$^{+4}$ is a smaller ion but perhaps a more difficult oxidation state to stabilize.

To improve on the La-based materials and to find new oxide functionality, we explored the ability of other materials to incorporate precious metals reversibly. One important modification scheme has been the use of large A- and B-site cations, to increase the unit cell volume. It has been shown that large cations can yield perovskite oxides that function well as either proton or oxygen ion conductors \cite{15,16}, the most promising being doped BC. The presence of large ions ($r_{\text{Ba}}=1.61$ Å and $r_{\text{Ce}}=0.87$ Å) on both A- and B-sites makes the host perovskite cell unusually large, and we propose that this large volume can more readily accommodate precious metal ions.

Another important perovskite design strategy pursued in this work is the use of an ionic, low-valence A-site cation (Ba), in order to stabilize higher redox states in adjacent cations, in this case the cation incorporation of Pd. The large size of BC and the redox-stabilization of Ba make BC a suitable host for precious metal dopants. We recently investigated \cite{17,18} how these design principles apply to Pd-doped BC, namely whether BCP reversibly incorporates Pd and whether it is an active catalyst.

$\text{BaCeO}_3$ has $t=0.94$ and is predicted to be an antiferrodistortive dielectric material. Since Ce$^{4+}$ and Pd$^{+2}$ have the same ionic radii in 6-fold coordination, Pd doping maintains $t$ and should not induce much strain. To
maintain charge neutrality, Pd^{2+} would need to be accompanied by an oxygen vacancy.

In this study, we examine the atomic and electronic properties of Pd-doped BC in detail using DFT. The local bonding environments around Pd as well as the electron fillings of atomic orbitals on Pd and its neighbors are examined. A particular focus is the character of the highest occupied molecular orbital (HOMO) and the few lowest unoccupied molecular orbitals (LUMO). These electronic states are compared with expectations based on crystal field splittings in the computed atomic geometries. This combined structural and electronic computational study helps explain the Pd incorporation previously reported.

There are several theoretical studies of pure BaCeO_{3} and with various dopants [19-22], but none of these reported theoretical predictions of the full ground state structure and symmetry group of pure BaCeO_{3} using DFT. Our preliminary theoretical studies are the first to consider Pd doping of BaCeO_{3}, which agree well with recently published experimental data [17, 18]. In this paper we investigate the atomic and electronic structure of BaCeO_{3} and BaCe_{1-x}Pd_{x}O_{3} in more depth, building upon previously reported results.

II. METHODOLOGY

In this study, an in-house solid state DFT code employed in previous studies [23, 24] is used to relax the ionic positions and optimize lattice constants. The generalized gradient approximation (GGA) [25] of the exchange correlation functional and a 4 x 4 x 4 Monkhorst-Pack sampling of the Brillouin zone [26] are used for all calculations. All atoms are represented by norm-conserving optimized [27] design nonlocal [28] pseudopotentials. All pseudopotentials are generated by the OPIUM code [29]. The calculations are performed with a plane wave cutoff of 50 Ry. Undoped and Pd-doped BaCeO_{3} calculations were performed on forty atom unit cells in a 2 x 2 x 2 supercell arrangement allowing for the three-dimensional octahedral tilt that is seen in experiment. In the Pd-doped perovskite, two supercells of composition BaCe_{0.875}Pd_{0.125}O_{2.875} were studied, as well as the structure containing no vacancy, BaCe_{0.875}Pd_{0.125}O_{3}. Structure 1 contains an O vacancy adjacent to Pd, and Structure 2 contains the vacancy in the next unit cell, between two Ce. Structure 3 contains no vacancy.

III. RESULTS

In the forty-atom BaCeO_{3} 2 x 2 x 2 unit cell, the O_{6} tilt angles are all 12.2°. However, the tilts along (100) and (001) are anti-phase and indistinguishable from each other, while the tilts along (010) are in-phase. This structure belongs to the Pnma symmetry group, and the forty-atom computational cell we used is a supercell of the primitive $\sqrt{2} \times 2 \times \sqrt{2}$ cell. Relaxed DFT lattice constants agree well with experiment [17], as seen in Table I as do the positions of ions from the experimental refinements.

Structures 1, 2, and 3 were modeled with $a = 8.799$, $b = 8.759$ and $c = 8.823$ Å , the relaxed DFT lattice constants of BaCe_{0.875}Pd_{0.125}O_{3} (Structure 3). Doping BaCeO_{3} with cationic Pd reduces the symmetry of the unit cell from Pnma to the space group P1. The tilt system in BaCeO_{3} is severely interrupted with the addition of one Pd, then becomes closer to the pure BC tilt pattern with the addition of a Pd-O vacancy pair. In Structure 3, the substitution of one Ce for one Pd with no accompanying vacancy has tilt angles that range from 2 to 15°. The average tilt angle of this system is 9.6 ± 4.6°. This perturbation results in a dramatic decrease in symmetry, also displayed by the Ce-O bond lengths. The three nearest Ce neighbors (Ce4, 6 and 7 in Table IV) all have two distinct sets of bond lengths; four bonds around 2.21 Å and two long bonds around 2.36 Å . The second nearest neighbors have six similar bond lengths of 2.28 Å on average. The three nearest Ce neighbors to Pd are enclosed within octahedra that distort, then tilt, as shown in Figure 3. The distorted Ce octahedra are the result of the formation of strong, short bonds (≈ 2.03 Å ) to the small Pd^{4+} cation. The bond lengths of 2.03 Å are typical of Pd^{4+} in an O_{6} environment ($r_{PD}$ =1.42 and $r_{PD^{4+}}$ =0.615).

Of the two structures with an oxygen vacancy, the higher energy structure is Structure 2, where the O vacancy is in between two Ce. This is 0.95 eV higher in energy than Structure 1, because the reduction of Pd^{4+} to Pd^{2+} is more favorable than the reduction of two Ce^{4+}. The vacancy in Structure 1 is further stabilized by the formation of a square planar environment around Pd^{2+}. As shown in Figure 1 the Pd in Structure 1 is four-coordinate square-planar, and not five-coordinate square-pyramidal. In a square-planar environment, $r_{PD^{2+}}$ = 0.64. This is supported by the Pd-O bond lengths in Structure 1 from Table I. The first four shortest bond lengths are on average 2.04 Å, and the fifth is 2.66 Å. This longer bond length occurs as a result of the apical O in the CeO_{3} square pyramid moving

| Parameter | Experiment | Theory |
|-----------|------------|--------|
| $a$       | 6.21       | 6.28   |
| $b$       | 8.77       | 8.81   |
| $c$       | 6.23       | 6.30   |
| Ba(x)     | 0.0207     | 0.0273 |
| Ba(z)     | -0.0075    | -0.0077|
| O1(x)     | -0.0132    | -0.020 |
| O1(z)     | 0.4250     | 0.4194 |
| O2(x)     | 0.2771     | 0.2833 |
| O2(y)     | 0.0383     | 0.0446 |
| O2(z)     | 0.7239     | 0.7184 |

TABLE I: Comparison of experimental [17] and theoretical structural parameters for BaCeO_{3}.
Ce1 2.26 2.27 2.27 2.27 2.32
Ce2 2.23 2.24 2.24 2.27 2.29
Ce3 2.23 2.24 2.24 2.25 2.28
Ce4 2.22 2.22 2.22 2.25 2.35 2.36
Ce5 2.24 2.24 2.25 2.27 2.28
Ce6 2.05 2.21 2.23 2.23 4.51
Ce7 2.22 2.22 2.22 2.25 2.35 2.35
Pd1 2.04 2.04 2.04 2.05 2.66 4.30

TABLE II: Six shortest B-O distances (in Å), for Structure 1, BaCe₀.₈₇₅Pd₀.₁₂₅O₂.₈₇₅, with vacancy between Pd1 and Ce6.

FIG. 1: Structure 1, where Pd dopant is adjacent to an O vacancy. This shows the lesser degree of octahedral distortion of the nearest neighbors when compared to Structure 2, as well as the increasingly symmetric tilt. Pd is green, Ba are light blue, Ce are gray and O red.

away from the Pd. This does not occur in Structure 2, where the vacancy is in between two Ce (Figure 2). All six Pd-O bond lengths in Structure 2 are around 2.02 Å, whereas the two CeO₅ surrounding the vacancy seem to contract inward, as seen from the bond lengths in Table III. These bond lengths are similar to those seen in Structure 3, where there is no vacancy.

This clearly indicates that Pd reduction via an O vacancy may be needed to alleviate some of the strain of this system induced by the small Pd⁴⁺ ion. When an O vacancy is placed between two Ce, as in Structure 2, the closest corner sharing octahedra decrease their tilt angles to either 9 or 2°. The remaining octahedra slightly increase their tilt angles to either 13 or 14°. Structure 2 is more distorted than Structure 3, and it seems to have less of a concerted tilt preference. The average tilt angle in Structure 2 is 9.9° ± 5.1°. In Structure 1, when the vacancy is between Pd and Ce, the corner sharing octahedra are not as affected, decreasing their tilt angles by at most 2°. The CeO₅ next to the vacancy decreases its tilt angle to 4°. The average tilt angle of Structure 1 is 9.9° ± 3.4°. The average tilt angle of Structures 1 and 2 is the same, but the standard deviation is larger for Structure 2. The largest interruption of concerted tilt systems by a vacancy occurs in Structure 2, where it is not stabilized by the Pd²⁺ cation. All four supercell structures resemble the tilt system a⁻⁻a⁺⁻⁻⁻, however symmetry has been broken by both the Pd substitution and accompanying O vacancy.

To elucidate the local structure of a disordered per-

Ce1 2.28 2.28 2.28 2.28 2.29 2.29
Ce2 2.23 2.24 2.26 2.26 2.27 2.27
Ce3 2.25 2.25 2.25 2.25 2.26 2.26
Ce4 2.20 2.20 2.22 2.22 2.36 2.36
Ce5 2.24 2.24 2.26 2.26 2.26 2.26
Ce6 2.21 2.21 2.21 2.21 2.37 2.37
Ce7 2.21 2.21 2.22 2.22 2.35 2.35
Pd1 2.03 2.03 2.03 2.03 2.04 2.04

FIG. 2: Structure 2 has an O vacancy between two Ce atoms, not adjacent to Pd (lower plane, not shown). Ba are light blue, Ce are gray and O red.

Ce1 2.21 2.22 2.22 2.22 2.24 4.34
Ce2 2.22 2.22 2.28 2.28 2.30 2.34
Ce3 2.17 2.21 2.21 2.22 2.23 4.34
Ce4 2.26 2.28 2.28 2.31 2.37 2.38
Ce5 2.22 2.22 2.26 2.27 2.32 2.35
Ce6 2.26 2.27 2.29 2.31 2.35 2.37
Ce7 2.22 2.22 2.22 2.22 2.36 2.42
Pd1 2.01 2.01 2.01 2.02 2.02 2.03

TABLE III: Six shortest B-O distances (in Å), for Structure 2 BaCe₀.₈₇₅Pd₀.₁₂₅O₂.₈₇₅, with vacancy in between Ce1 and Ce3.

Ce1 2.87
Ce2 2.87
Ce3 2.87
Ce4 2.87
Ce5 2.87
Ce6 2.87
Pd1 2.87

TABLE IV: Six shortest B-O distances (in Å), in Structure 3 BaCe₀.₈₇₅Pd₀.₁₂₅O₃, with no vacancies.

Ba are light blue, Ce are gray and O red.
FIG. 3: Structure 3, where Pd dopant is not accompanied by an O vacancy. Pd is green, Ba are light blue, Ce are gray and O red.

ovskite, such as BCP, we simulate a neutron-scattering pair distribution function (PDF) by combining DFT-computed atomic positions and known neutron scattering factors. To make direct comparison with experimental neutron PDF, we subtract the average number density and multiply by $4\pi r$:

$$G(r) = 4\pi r(\rho(r) - \rho_0(r))$$

(2)

where $\rho(r)$ is the microscopic pair density and $\rho_0(r)$ is the average number density. The experimental PDF $G(r)$ of BCP generated with the program PDFFIT [30] matches closely the DFT-derived PDF of Structure 1 generated by an in-house code used in previous studies [31, 32]. The correspondence in peaks, as shown in Figure 4, is strong, especially for short $r$. This further supports the agreement between experimental data and our calculations, as well as the assignment of Pd$^{2+}$ being stabilized by an O vacancy in Structure 1. The match between experiment and theory was much less close for PDFs generated from Structure 2 and Structure 3, providing evidence that Pd-vacancy pairs are present in the experimentally prepared BCP sample.

Analysis of the density of states (DOS) of the three structures shows that Structure 1 contains an interesting feature absent from either Structures 2 or 3. Above the Fermi level, there is a $d$-orbital localized on Pd that is $d_{x^2-y^2}$. This is shown in Figure 5(c) and indicates the presence of Pd$^{2+}$. This $d$-orbital is not present in either the HOMO (Figure 5(a)) or LUMO (Figure 5(b)). In a square-planar environment, this is the non-degenerate $d$-orbital that is highest in energy. It is absent from both Structures 2 and 3 because Pd instead assumes a Pd$^{4+}$ oxidation state in octahedral coordination.

A comparison of the projected density of states of the Pd $d$-orbitals in Figure 6 shows that the Pd in Structure 1 is different than the more similar Structures 2 and 3. Since Structures 2 and 3 both contain Pd$^{4+}$ in an octahedral environment, they have the same $d$-states, though shifted in energy. The Pd in Structure 2 is slightly more ionic than in Structure 3, an effect caused by the O vacancy in Structure 2. This O vacancy, in between two Ce, has caused the octahedron around Pd to contract slightly, forming stronger, more ionic, Pd-O bonds. In Structure 1, new $d$-states closer to the Fermi level are populated, and previously unfilled bands, above the Fermi level, decrease in intensity. This is because Pd has been stabilized in a square planar environment as Pd$^{2+}$. The shift of the $d$-states closer towards the Fermi level when compared to Structures 2 and 3 also support Pd being less ionic.

IV. CONCLUSION

We have presented here a DFT study of the ground state structures of the undoped and Pd-doped rare-earth perovskite BaCeO$_3$. The Wyckoff positions and space group assignment for BaCeO$_3$ are in agreement with experiment. The substitution of Ce by Pd without an accompanying O vacancy distorts the doped perovskite moreso than with an accompanying vacancy. When the vacancy is not adjacent to Pd, but is between two Ce, the structure is less stable. Located between a Pd-Ce pair, the vacancy causes the CeO$_5$ square pyramid to tilt away from Pd, stabilizing a four-coordinate square-planar Pd geometry. The stabilization is about 0.95 eV relative to Structure 2. The coordination of Pd is also supported in the position of filled Pd $d$-states just below the Fermi level of Structure 1 that are not filled in either Structures...
FIG. 5: a) The HOMO of Structure 1, where the electron density is localized around the Pd cation, and its nearest Ce neighbors. b) The LUMO of Structure 1, composed solely of Ce f-orbitals. There is no electron density localized around Pd. c) An empty state above the LUMO, composed of Ce f-orbitals and a Pd d_{x^2-y^2}. In all figures, Pd is the green cation located at the right corner, Ce are white, Ba are light blue and O red. Bonds are omitted for clarity of the isosurface shown.

FIG. 6: Projected Density of States of the Pd d-states. Structure 1 (top) shows that a filled band is being stabilized when an oxygen vacancy is placed between a Pd-Ce pair, as d-states above the Fermi level become less populated. This feature is not seen in either Structures 2 (middle) or 3 (bottom). In these two structures, there appear sharply intense bands around -5 eV, absent in Structure 1. These are filled states, lower in energy, that demonstrate the more ionic nature of the Pd in Structures 2 and 3.

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