Thermodynamic properties of neutral and charged oxygen vacancies in BaZrO$_3$ based on first principles phonon calculations

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The structural, electronic and thermodynamic properties of neutral (v$^0_0$) and positively doubly charged (v$^{2+}_0$) oxygen vacancies in BaZrO$_3$ are addressed by first principles phonon calculations. The calculations are performed using two complementary first principles approaches and functionals; the linear combination of atomic orbitals (LCAO) within the hybrid Hartree–Fock and density functional theory formalism (HF–DFT), and the projector augmented plane wave approach (PAW) within DFT. Phonons are shown to contribute significantly to the formation energy of the charged oxygen vacancy at high temperatures (∼1 eV at 1000 K), due to both its large distortion of the local structure, and its large negative formation volume. For the neutral vacancy, the resulting lattice distortions, and thus the contributions from phonons to the free formation energy, are significantly smaller. As a result, phonons affect the relative stability of the two defects at finite temperatures and the charge transition level for oxygen vacancies (+2/0) changes from 0.42 to 0.83 eV below the conduction band bottom from 0 K to 1000 K.

1. Introduction

ABO$_3$-type perovskite structured oxides comprise a broad family of technologically important materials which display a wide range of functional properties, such as ferroelectricity, magnetism, their combination (multiferroics), piezoelectricity, high-temperature superconductivity, mixed ionic-electronic conductivity and electro-optic effects.$^1$–$^4$ Oxygen vacancies are common point defects in these materials and have been shown to influence a variety of properties, such as mechanical$^5$ and optical properties,$^6$–$^8$ as well as ionic conductivity.$^9,^10$

BaZrO$_3$ is a cubic perovskite that has attracted considerable attention in recent years for its possible application as dielectric material for wireless communication devices,$^{11}$ hybrid perovskite–polymer–magnetic nanocomposites$^{12}$ and as a substrate for thin films.$^{13}$ Additionally, Y-doped BaZrO$_3$ is a promising candidate material for protonic ceramic fuel cells operating in the range of 400–700 °C due to its high solid state proton conductivity.$^{14}$–$^{16}$ Working at intermediate temperatures improves device durability and compatibility between components and is thus more favorable than operating at the usual temperature range of 800–1000 °C of ceramic solid oxides fuel cells.$^{17}$ In addition, Y-doped BaZrO$_3$ may be used in other electrochemical applications such as sensors and hydrogen pumps.$^{18}$ The proton conductivity arises from incorporation of protons in the doped material by dissociative absorption of water molecules upon exposure to humid atmospheres.$^{14}$ Thus, fully ionized oxygen vacancies (v$^{2+}_0$) play here a crucial role. Although charged vacancies dominate acceptor doped oxides, vacancies with two trapped electrons (v$^{0}_0$, the color F centers) are more common in undoped oxides under reducing conditions, where the electron chemical potential is higher, or at lower temperature, where Coulomb attraction plays a greater role.$^{7,^8,^19}$–$^{21}$ The two charge states of the oxygen vacancy (v$^{2+}_0$ and v$^0_0$) represent the limiting cases in partly ionic and covalent perovskites, where electrons are neither fully localized in the oxygen vacancy by electrostatic fields, as in more ionic compounds like MgO, nor are completely localized on the dangling bonds of the nearest cations, as in more covalent materials, such as silicates.

Density functional approaches have in the recent decade been shown to be vital in defect analyses of functional oxides, and are now routinely applied in investigations of electronic properties and defect thermodynamics. The majority of such investigations, however, consider the thermodynamic properties of defects only at zero K, while most physical and chemical processes occur at moderate or high temperatures.

An important contribution to the thermodynamic properties at finite temperatures is the vibrational partition function,
which can be evaluated by calculating the material’s normal modes of lattice vibrations. Several authors have previously addressed the vibrational contribution to thermodynamic properties of oxygen vacancies in perovskites, such as SrTiO₃, and the complex La₁₋ₓSrₓCo₀.₅Fe₀.₅O₃, but there are still few reports on BaZrO₃. Sundell et al. addressed defect entropies in BaZrO₃ from a computational perspective using the simplified Einstein model, but considered only the contributions due to changes in the vibrational properties of the eight oxygen atoms nearest to the charged oxygen vacancy, thereby neglecting long range and volume relaxation effects. Recently, we performed complete phonon analyses of v_0 and protonic defects (OH⁻) in BaZrO₃ using a plane-wave pseudopotential approach at the GGA level, showing that phonons have a significant impact on the thermodynamics of v_0.

Calculations of vibrational frequencies may also reveal structural instabilities through low frequency or imaginary phonon frequencies, allowing for identification of eventual soft modes that are responsible for phase transitions, such as in SrTiO₃. According to experimental X-ray and neutron powder diffraction analyses, BaZrO₃ does not undergo any phase transition down to 2 K. First principles studies of BaZrO₃ using the LDA and GGA exchange–correlation functionals have, however, indicated structural instabilities at the R- and/or M-points of the BZ that would lead to an antiferrodistortive transition at low temperatures, as in SrTiO₃. Ilčič and Gale pointed out that the same functional (PW91) gives different results depending on the employed pseudopotentials; for example, for plane-waves basis set calculations performed using VASP, soft-USP, standard-USP, standard-PAW and hard-PAW O potentials predict a stable cubic structure, while the soft-PAW O potential suggests an antiferrodistortive transition. This disagreement with experiments has been suggested to stem from neglect of zero-point contributions and/or anharmonic effects, which could suppress the phase transition. On the other hand, the employment of the hybrid PBE0 functional has shown a significantly better agreement with the experimental frequencies at the Γ-point of the BZ and the absence of imaginary modes at any of the high symmetry q-points. These contradictory results illustrate the importance of a suitable choice of computational approach when evaluating the vibrational properties of, especially, perovskite structured oxides. The hybrid functionals were successfully used recently in the study of oxygen vacancies in Ti- and Zr-based perovskites, e.g. ref. 7 and 31.

In this study, we therefore employ two complementary ab initio methods: the linear combination of atomic orbitals (LCAO) and the plane-wave method within the projector augmented wave (PAW) approach, employing the hybrid HF-DFT PBE0 functional and standard DFT functionals (PBE and RPBE) for a complete investigation of the structural, electronic and vibrational properties of oxygen vacancies in the two different charge states, 0 or +2, in bulk BaZrO₃. The pure DFT functionals are included for comparison as they are more computationally applicable to large scale calculations than the PBE0 method. Particular emphasis is given to the effect of the computational method on the vibrational contributions to the defect thermodynamic properties, and the effect of the vibrational contributions on the relative stability of the two oxygen vacancy charge states.

2. Computational details

The calculations performed in this contribution can be divided in two main categories; localized basis sets (LCAO) and the hybrid HF-DFT Perdew–Burke–Ernzerhof exchange–correlation functional (PBE0), performed using the CRYSTAL14 code, and plane-wave basis set employing the PAW method using the PBE and RPBE exchange–correlation functionals as implemented in the VASP code (version 5.3.5). Calculations using CRYSTAL were mainly performed using two atomic basis sets (BSs) consisting of Gaussian-type functions with pseudopotentials. The two BSs (hereafter, BS1 and BS2) were used for comparison and deeper analysis of the main results. BS1 included quasi-relativistic pseudopotentials taken from the pseudopotential library of the Stuttgart/Cologne group, with 46 core electrons of Ba and 28 core electrons of Zr. In order to avoid spurious interactions between the diffuse functions and the core functions of neighboring atoms, the BS1 diffuse exponents smaller than 0.1 bohr⁻² were removed as well as f-electron virtual functions. The Gaussian BS and Hay–Wadt small core pseudopotentials for Ba[311(1d)G] and Zr[311d31G] in BS2 were taken from the CRYSTAL website. In both BS1 and BS2 the all-electron BS 8-411G was used for O atoms. Only BS1 was employed in the calculations involving defective BaZrO₃. The tolerance factors of 7,7,7,7 and 14 for the Coulomb and exchange integrals were used in CRYSTAL calculations. For all the studied defects, we considered only the closed shell electronic configuration, and the SCF threshold value for energy convergence was set to 10⁻⁷ eV. The high frequency dielectric constant (εₓ) was calculated using the coupled perturbed Kohn–Sham method implemented in the code, the Born effective charges tensor was numerically evaluated through the Berry phase approach.

In VASP, the core potentials were treated using the projector augmented wave method (PAW), while the valence configurations for Ba, Zr and O were taken as 5s²5p⁶5d², 4s²4p⁶4d²5s² and 2s²2p⁴, respectively, with a constant plane-wave cut-off energy of 500 eV. To ensure sufficient convergence of the calculated forces, all calculations were performed using a reciprocal projection scheme with ionic and electronic convergence criteria of 10⁻⁴ eV Å⁻¹ and 10⁻⁸ eV, respectively. Finally, Born effective charges and the static dielectric tensor were determined in the independent particle approximation through density functional perturbation theory.

In VASP, v_0 was modelled by removing a single O atom, whereas in CRYSTAL the BS of the vacant oxygen ion was maintained by means of a spurious “ghost” atom BS with no atomic mass. The latter approach allows for localization of electrons within the vacancy itself. In both VASP and CRYSTAL, v_0 was modelled by removing two electrons from the overall supercell through charge compensation by a homogeneous jellium background charge. Calculations were performed with...
2 x 2 x 2 (40 atoms) and 3 x 3 x 3 (135 atoms) supercell expansions of the 5-atom primitive cubic cell of BaZrO$_3$, corresponding to defect concentrations of 12.5% and 3.7%, respectively. Electronic integration over the BZ was performed using a 8 x 8 x 8 Monkhorst–Pack $k$-mesh for the 5-atom unit cell. For supercell expansions, the $k$-mesh density was reduced accordingly. With both CRYSTAL and VASP, all defect calculations were performed by allowing volume and shape relaxations, and the thermodynamic quantities therefore represent the constant pressure situation.

Vibrational frequencies were calculated within the harmonic approximation by numerical evaluation of the dynamical matrix elements using the first derivative of the atomic energy gradients, displacing each atom along the Cartesian coordinates by 0.001 Å for BS1 and 0.01 Å for BS2 in CRYSTAL (technical details can be found in ref. 47 and 48) and by 0.005 Å in VASP (the numerical evaluation was performed using the Phonon code$^{49}$).

The fundamental quantity determining the thermodynamic stability of a defect is its free energy of formation, which, in accordance with the formalism suggested by Zhang and Northrup$^{50}$, improved in the present study including vibrational contributions, for an oxygen vacancy in charge state $q$ takes the form:

$$\Delta G_{v, q}(T) = G_{v, q}(T) - G_{\text{perfect}}(T) + \mu_{O}(T, p_{O_2}) + q(\mu_{e} + \Delta \varepsilon_e) + E_{\text{corr}}.$$  

\(G_{v, q}(T)\) and \(G_{\text{perfect}}(T)\) are the Gibbs free energy of the defective and non-defective systems, respectively, while \(\mu_{O}(T, p_{O_2})\) and \(\mu_{e}\) are the chemical potentials of oxygen and electrons. \(\Delta \varepsilon_e\) aligns the Fermi levels of the charged defective and neutral cells based on the difference in the electrostatic core potentials induced by the charge-compensating jellium background.$^{51}$ Suitable correction terms to account for finite size errors stemming from e.g. electrostatic and elastic interactions may be included in $E_{\text{corr}}$ (not included here).$^{52}$ Further, $\mu_{O}(T, p_{O_2})$ is taken as half that of the O$_2$ molecule:

$$\mu_{O}(T, p_{O_2}) = 0.5\left( E_{\text{el}}^{O_2} + E_{\text{opt}}^{O_2} + H^{\infty}_{O_2}(T) - TS_{O_2}^{\infty}(T) \right) + k_{B} T \ln(p_{O_2}/p^\infty).$$

$\mu_{O}(T, p_{O_2})$ is mainly used in our VASP/PBE calculations, which is known to overestimate the binding energy of the O$_2$ molecule (cf. ref. 53). Different approaches exist in the literature,$^{24,51}$ in order to correct this overbinding, and account for the temperature dependence of $\mu_{O}$. We have chosen a correction term of 1.36 eV per O$_2$ (as determined by Lee et al.$^{53}$) and added it to $E_{\text{el}}^{O_2}$. The zero-point energy of O$_2$(E$_{\text{opt}}^{\infty}$) was taken as 98 meV, corresponding to the experimental O–O frequency. $H^{\infty}_{O_2}(T)$ and $S^{\infty}_{O_2}(T)$ were further determined from tabulated values$^{54}$ by integrating the heat capacity data from zero temperature to the temperature of interest. For electrons, $\mu_{e}$ may take values from the top of the valence band to the bottom of the conduction band.

As the main focus of this work is to determine the contribution from phonons to the Gibbs free energy of defect formation, it is convenient to separate $\Delta G_{v, q}(T)$ into electronic, vibrational and gas phase contributions:

$$\Delta G_{v, q}(T) = \Delta E_{\text{el}} + \Delta S^{\text{vib}}(T) - T \Delta S^{\text{vib}}(T)$$

$$+ 0.5 \left( E_{O_2}^{\text{el}} + E_{O_2}^{\text{opt}} + H^{\infty}_{O_2}(T) - TS^{\infty}_{O_2}(T) \right)$$

where $\Delta E^{\text{vib}}(T)$ and $\Delta S^{\text{vib}}(T)$ contain the contribution from phonons to the free energy of the solid. $\Delta$ indicates the difference between quantities for the defective and non-defective systems. Thus, $E^{\text{vib}}$ and $S^{\text{vib}}$ for the solid phase are computed from all symmetrized harmonic vibrational frequencies $\nu_s(q)$, $s = 1, 2, \ldots, 3N$, where $N$ is the number of atoms in the unit cell and $q$ is the reciprocal lattice vector in the first Brillouin zone according to:

$$G^{\text{vib}}(T) = \sum_{s, q} \left( \frac{n_{s, q}(T)}{2} \right) \hbar \nu_s(q)$$

$$- T \sum_{s, q} \left( \frac{n_{s, q}(T)}{2} \right) \hbar \nu_s(q) - k_{B} \ln \left( 1 - e^{-\hbar \nu_s(q)/k_{B} T} \right) + pV,$$

where the first sum represents the vibrational internal energy, $U^{\text{vib}}$ (zero point energy included), and the second represents the vibrational entropy, $S^{\text{vib}}$. $n_{s, q}$ is the Bose–Einstein distribution

$$\frac{1}{e^{\nu_s(q)/k_{B} T} - 1}$$

and $pV$ is the product between the system pressure and volume.

$G^{\text{vib}}$ should be evaluated by summation over all possible $q$-points, but as this requires expansion of the supercell, defect formation energies were only evaluated by considering frequencies at the $\Gamma$-point of the Brillouin zone (BZ) of the defective supercells. For the non-defective system, however, we evaluate the phonon dispersions by 2 x 2 x 2 and 3 x 3 x 3 supercell expansions of the primitive unit cell, thus including calculation of the frequencies at the $\Gamma$-point, plus 7 $q$-points at $M$, $X$ and $R$, and at the $\Gamma$-point plus 26 $q$-points along the $\Delta$, $\Sigma$ and $\Lambda$ directions, respectively.

3. Results and discussion

Pristine BaZrO$_3$

Table 1 compares various bulk properties of BaZrO$_3$ calculated using CRYSTAL/PBE0 and VASP/PBE or RPBE in this work, and selected literature reports. The lattice parameters are in general in good agreement with the experimental value of 4.192 Å.$^{55}$ The PBE and RPBE functionals, however, predict somewhat larger lattice parameters than the hybrid PBE0 functional, except for the study$^{56}$ where the PW91 was applied. This is reflected by the slightly shorter interatomic bonding distances calculated using the PBE0 functional than with the pure DFT functionals. CRYSTAL/CRYSTAL using BS1 yields an indirect band gap ($M \rightarrow T$) of 5.36 eV, being in good agreement with the experimental value of 5.33 eV.$^{57}$ The value obtained using BS2 is slightly underestimated whereas the hybrid B3LYP functional noticeably
and their experimental values. Due to calculated using CRYSTAL/PBE0 and VASP/PBE (including the partial ionic character of BaZrO$_3$. Moreover, the calculations show an overlap population charge of 68 me for the Zr–O bond, indicative of larger covalent character of the former bond. The Born effective charges are in addition comparable between VASP and CRYSTAL, irrespective of the functional.

We calculated the high frequency (electronic part) and static (electronic plus ionic part) dielectric constants in order to evaluate the splitting between longitudinal and transversal optical vibrational modes. The calculated dielectric constant is in good agreement with the experimental value of 38.4,59 and the two different BSs used in CRYSTAL give similar results.

Table 2 reports the vibrational frequencies at the Γ-point calculated using CRYSTAL/PBE0 and VASP/PBE (including the T.O.–L.O. splitting), and their experimental values. Due to the cubic symmetry of BaZrO$_3$ (space group $O_h$ number 221), one obtains the following set of optical phonon modes at the $\Gamma$-point: $4t_{1u} + t_{2u}$. The results obtained using CRYSTAL and VASP are comparable and in good agreement with the experimental values. The Zr–O$_3$ torsion mode is both IR and Raman inactive (silent mode of $t_{2u}$ symmetry) and cannot be detected experimentally. In particular, due to the cubic symmetry, there are no Raman allowed vibrational modes in BaZrO$_3$ and thus the L.O. frequencies are not detectable from experiments. Although the T.O.–L.O. splitting is pronounced, we found that its contribution to the thermodynamic potentials is negligible ($\gamma^{\text{ab}}$ increases at maximum 0.1 eV in the range 0–1600 K), and was thus not accounted for in the defect calculations. To further investigate the vibrational properties and structural stability of BaZrO$_3$, we calculated the phonon dispersion relationship along the $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma \rightarrow R \rightarrow M \rightarrow \Gamma$ path in the BZ. The dispersion curves in Fig. 1 were obtained by interpolating the discrete points obtained using a $2 \times 2 \times 2$ supercell expansion. There is a notable effect of the choice of code and functional, especially on the low frequency modes at the $R$-point, which correspond to rotation of the ZrO$_6$ octahedra and are related to the stability of the cubic structure. Using VASP, the lowest frequency obtained at the $R$-point is 17 and 44 cm$^{-1}$ for PBE and RPBE functionals, respectively, while using CRYSTAL/PBE0 and BS1 the frequency is 63 cm$^{-1}$. In general, the frequencies obtained using the PBE or RPBE functional in VASP are lower than those obtained using CRYSTAL/PBE0, in line with the larger lattice parameters. In addition, a comparison of two BSs used in CRYSTAL revealed a similar trend of the phonon frequencies, i.e. a larger volume of the unit cell predicted using BS2 gives softer frequencies (e.g. 41 vs. 63 cm$^{-1}$ at the $R$-point and 120 vs. 125 cm$^{-1}$ at the $\Gamma$-point). The frequencies obtained using CRYSTAL/PBE0 are also in good agreement with those reported by Evarestov$^{30}$ employing the same code and functional. The study of phonon frequencies in BaZrO$_3$ reported in ref. 26 and 27 where the LDA functional was employed showed imaginary frequencies at the $R$- and/or $M$-points. Furthermore, in ref. 28 the GGA-PW91 functional in VASP revealed no instabilities for the cubic structure of BaZrO$_3$. We, however, find that the GGA-PW91 functionals underestimate it.

Table 1. Lattice parameter ($a$), bonding lengths ($d$), Mulliken atomic charges in LCAO, Born effective charges ($Z_{\text{Born}}$), electronic ($\varepsilon_e$) and static ($\varepsilon_0$) dielectric constants, and the band gap ($\Delta E_g$). The values are compared with different computational and experimental studies from literature. The values in parentheses refer to BS2

<table>
<thead>
<tr>
<th>Mode</th>
<th>LCAO (BS1)</th>
<th>PW (BS1)</th>
<th>PW (BS2)</th>
<th>PW (Expt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d$(Zr–O)/Å</td>
<td>2.098</td>
<td>2.118</td>
<td>2.135</td>
<td>2.135</td>
</tr>
<tr>
<td>$d$(Ba–O)/Å</td>
<td>2.966</td>
<td>2.995</td>
<td>3.019</td>
<td>3.019</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>4.195 (4.217)</td>
<td>4.235</td>
<td>4.269</td>
<td>4.207$^{28}$</td>
</tr>
<tr>
<td>$\varepsilon_e$</td>
<td>1.32</td>
<td>1.95</td>
<td>1.94</td>
<td>1.99</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>2.63</td>
<td>6.13</td>
<td>6.05$^{28}$</td>
<td>4.8$^{28}$</td>
</tr>
<tr>
<td>$\Delta E_g$/eV</td>
<td>3.56</td>
<td>3.12</td>
<td>3.11</td>
<td>3.84$^{59}$</td>
</tr>
<tr>
<td>$\Delta E_g$/eV</td>
<td>5.16</td>
<td>5.4</td>
<td>4.79</td>
<td>5.33$^{57}$</td>
</tr>
</tbody>
</table>

* Current study.
Table 3. Relative lattice constant ($\Delta a/a_0$, $\Delta b/b_0$, $\Delta c/c_0$) and bond distance relaxations ($\Delta d$), formation volume ($\Delta V$), relative volume relaxation ($\Delta V/V_0$), the minimum distance between the conduction band minimum and the defective level ($\Delta E$) and the defect band width ($\delta E$) of $\nu_o$ and $\nu^{**}_o$, calculated using CRYSTAL/PBE0 and VASP/PBE using $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercell expansions. The relative relaxations are given as percentile relative expansion per mole fraction of oxygen vacancies. In accordance with local site symmetry of oxygens (point group symmetry $D_{0}$), the symmetry of the defective supercells is lowered to $D_{4h}$.

<table>
<thead>
<tr>
<th>Code</th>
<th>CRYSTAL (PBE0)</th>
<th>VASP (PBE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen vacancy</td>
<td>$\nu_o$</td>
<td>$\nu^{**}_o$</td>
</tr>
<tr>
<td>$\Delta a/a_0$ (%)</td>
<td>$-0.29$</td>
<td>$-13.4$</td>
</tr>
<tr>
<td>$\Delta b/b_0$ (%)</td>
<td>$-0.29$</td>
<td>$-13.4$</td>
</tr>
<tr>
<td>$\Delta c/c_0$ (%)</td>
<td>$-0.88$</td>
<td>$-10.6$</td>
</tr>
<tr>
<td>$\Delta d(Zr-vO)/d_o(Zr-O)$ (%)</td>
<td>$-0.01$</td>
<td>$1.34$</td>
</tr>
<tr>
<td>$\Delta d(Ba-vO)/d_o(Ba-O)$ (%)</td>
<td>$-0.92$</td>
<td>$-6.86$</td>
</tr>
<tr>
<td>$\Delta V/V_0$ (%)</td>
<td>$-1.07$</td>
<td>$-27.1$</td>
</tr>
<tr>
<td>$\Delta E$ (eV)</td>
<td>$1.45$</td>
<td>$-37.3$</td>
</tr>
<tr>
<td>$\delta E$ (eV)</td>
<td>$1.31$</td>
<td>$0.20$</td>
</tr>
</tbody>
</table>

Functional in VASP, in addition to the LDA, PBEsol and AM05 functionals, resulted in imaginary modes at the $R$- and/or $M$-points. Hence, only the PBE and RPBE functionals in VASP predict a stable cubic structure for BaZrO$_3$.

Neutral and charged oxygen vacancies: atomic and electronic properties

Table 3 shows structural relaxations induced by $\nu_o$ and $\nu^{**}_o$ in CRYSTAL/PBE0 and VASP/PBE calculations using $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercell expansions. $\nu_o$ only results in small relaxations using both methods and for both defect concentrations. There are, however, subtle differences in the equilibrium structure obtained with the two codes. CRYSTAL predicts a minor contraction of the $a/b$-axis (normal to the Zr-$vO$-Zr axis, see the atomic arrangement in Fig. 2), and expansion of the $c$-axis (parallel to the Zr-$vO$-Zr axis, see Fig. 2) for both defect concentrations, and thus a slight expansion of the overall unit cell. Using CRYSTAL, however, the $\nu_o$ leads to a slight contraction of the cell for both defect concentrations. We suggest that this subtle effect is related to the inclusion of the “ghost” basis functions in the vacancy in CRYSTAL. In order to decrease the energy of the defect-induced level (the position of the defect-induced level on the band structure, Fig. 3), the $c$-axis shrinks in order to maximize the overlap between the “ghost”
orbitals, and the p and d orbitals of the nearest Zr atoms. In addition, we performed a test calculation using CRYSTAL leaving vacuum (i.e. no “ghost” basis functions) in the $v'_0$ and noticed that the $c$-axis, and in particular the distances between Zr atoms in the Zr-$v'_0$-Zr complex, expand somewhat. In accordance with VASP calculations, we found that the other two axes shrink, but the magnitude of the contraction was larger in CRYSTAL and the overall effect on the supercell structure is a volume reduction larger than in the case where “ghost” orbitals were used. Nevertheless, a comparison of our results obtained with CRYSTAL for the two cases, i.e. using ghost functions and leaving vacuum in the vacancy position, revealed a lower formation energy of the oxygen vacancy for the former approach.

Upon using both CRYSTAL/PBE0 and VASP/PBE, the new band induced by $v'_0$ is fully occupied (see Fig. 3), with its maximum occurring at the $M$-point of the first BZ and situated below the conduction band. In CRYSTAL/PBE0, the band is located deep in the band gap, with a minimum distance of 1.31 eV (1.58 eV in the $3 \times 3 \times 3$ supercell) to the conduction band minimum, in agreement with previous reports of deep F-center induced defect levels in zirconate perovskites modelled with a “ghost” BS. In VASP/PBE, however, the band occurs significantly closer to the conduction band (Table 3), and the top of the defect level at the $R$-point almost overlaps with the conduction band minimum at the $I$-point. The F-center partly reduces the two nearest Zr atoms, as the two electrons in the defect level are mostly localized on their d-states (Fig. 3). This is also in line with the literature for other oxides. In contrast, the use of the ghost BS for $v'_0$ leads to a high localization of the electronic charge density on the vacancy s-type ghost orbitals (Fig. 3); the Mulliken analysis shows 1 e being trapped within the vacancy whereas the Zr d-states do not contribute to the defect level. Without the ghost BS in the CRYSTAL calculations, the electrons also tend to localize in the vacancy, however, with a preference for the nearest Zr p, d orbitals (Fig. 3) which is not energetically favorable from the viewpoint of the defect formation energy.

For $v''_0$, Mulliken charge analyses performed using CRYSTAL indicated a small charge of merely 0.2 e associated with the vacancy ghost BS; hence the site is effectively positively charged and repels the nearest Zr and Ba cations, while it attracts the nearest oxide anions. This is clearly reflected by the structural arrangement of $v'_0$ and $v''_0$, as shown in Table 3 and in Fig. 2 ($3 \times 3 \times 3$ supercell using VASP, PBE). In particular, $v''_0$ induces a large outward displacement of the two nearest Zr ions, resulting in an anisotropic relaxation that yields a tetragonal defective cell. The inward relaxation of the 8 nearest O ions is significantly larger for $v''_0$ than $v'_0$, resulting in a general contraction in all directions, and thus a large negative formation volume. Using CRYSTAL/PBE0, the formation volume and inward relaxations are somewhat larger than VASP/PBE, which possibly is an effect of the difference in the employed potentials. Finally, the anisotropic relaxations induced by the oxygen vacancies reduce the symmetry of defective supercells to $D_{4h}(123)$.

For the $v''_0$, the defect induced band is unoccupied and lies much closer to the conduction band bottom compared to the

**Fig. 3** Top: band structure of the $2 \times 2 \times 2$ BaZrO$_3$ supercell with a $v'_0$ calculated using CRYSTAL (left) and VASP (right); bottom: electronic charge density of $v'_0$ projected on the defect level obtained using CRYSTAL using the ghost BS (left) or without the ghost BS (right). The isosurface threshold level is set to 0.002 e per $a_0^3$ (warmer color indicates increasing charge density).
neutral defect. Using CRystal/PBE0, the minimum distance between this band and the conduction band bottom is only 0.20 eV for both supercell sizes, while with VASP it completely overlaps with the conduction band states.

Neutral and charged oxygen vacancies: thermodynamics

Fig. 4 shows the vibrational density of states (DOS) for $v_O$ and $v_O^+$ calculated using the $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells in CRystal. Both defects induce a distinguishable vibrational peak at around 660 cm$^{-1}$ in the $2 \times 2 \times 2$ supercell, and 676 cm$^{-1}$ and 630 cm$^{-1}$ in the $3 \times 3 \times 3$ supercell for $v_O$ and $v_O^+$, respectively, originating from the Zr–O stretch of the two Zr atoms closest to the vacancy. This mode belongs to the $A_1$ irreducible representation of the space group and is thus both IR and Raman active. Its IR intensities, evaluated using the Berry phase approach, are 446 km mol$^{-1}$ ($2 \times 2 \times 2$ supercell) and 464 km mol$^{-1}$ ($3 \times 3 \times 3$ supercell) for $v_O^+$, and around 704 km mol$^{-1}$ ($2 \times 2 \times 2$ supercell) and 1394 km mol$^{-1}$ ($3 \times 3 \times 3$ supercell) for $v_O^+$, and should therefore be detectable in experiments. These results agree with those of a previous study on SrTiO$_3$ showing a vibrational mode at around 630 cm$^{-1}$ for $v_O^+$, corresponding to the relative motion of Ti and O atoms near the vacancy. In addition, the large negative formation volume of $v_O^+$ leads to stiffening of the bonds and thus a general blue-shift of all vibrational frequencies.

Fig. 5 shows the corresponding phonon contribution to the formation enthalpy and entropy of $v_O$ and $v_O^+$ calculated using CRystal/PBE0 and VASP/PBE using both $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells. At $T = 0$ K, the only contribution to $\Delta H^{vib}$ is the difference in the zero-point energy between the defective and perfect supercells. For $v_O$, $\Delta H^{vib} < 0$ at 0 K using both supercells, as expected due to the removal of 3 vibrational degrees of freedom upon vacancy formation. For $v_O^+$, however, $\Delta H^{vib} > 0$ at 0 K, which stems from the blue-shift of the phonon spectrum due to the considerable negative formation volume.

Furthermore, $\Delta H^{vib}$ decreases with increasing temperature for both charge states, reflecting a negative contribution from phonons to the formation entropy. CRystal and VASP further yield similar $\Delta H^{vib}$ for both charge states using the $3 \times 3 \times 3$ supercell, while CRystal yields slightly higher values than VASP employing the smallest supercell. This is a consequence of the larger blue shift found using CRystal in the $2 \times 2 \times 2$ than in the $3 \times 3 \times 3$ supercell, which slightly increases the enthalpy of the defective system. The shift is more pronounced for $v_O^+$ and therefore $\Delta H^{vib}_{(O_{1}\rightarrow O_{2})}(0 \text{ K})$ is around 0.08 eV larger in the smaller supercell than in the larger; while for $v_O$ the difference in $\Delta H^{vib}_{(v_O,0)}(0 \text{ K})$ is merely 0.03 eV.

The calculated $\Delta S^{vib}$ is negative for both $v_O$ and $v_O^+$, and comparable with CRystal/PBE0 and VASP/PBE results. In CRystal/PBE0, $\Delta S^{vib}$ is not affected by the supercell size and its value is modest for $v_O^+$ within the considered temperature range, as expected from the negligible effect of $v_O^+$ on the PDOS. On the other hand, $\Delta H^{vib}$ is somewhat larger (more negative) using the $3 \times 3 \times 3$ than the $2 \times 2 \times 2$ supercell (with CRystal), due to the larger number of vibrational modes and the wider local structural relaxation allowed by the former supercell. VASP/PBE predicts a more negative $\Delta S^{vib}$ of both defects using the $2 \times 2 \times 2$ supercell, which arises from an overestimated contribution due to extinction of the low frequency modes at the $\Gamma$-point, which are not sampled using the $3 \times 3 \times 3$ supercell. Using the $3 \times 3 \times 3$ supercell, the $\Delta S^{vib}$ are slightly more negative in CRystal/PBE0 than VASP/PBE, which stems from the greater inward relaxations of both defects using the former approach. Finally, using the RPBE functional in VASP, the $\Delta S^{vib}$ was nearly identical to the PBE value calculated using the $3 \times 3 \times 3$ supercell with both supercells. Hence, PBE and RPBE with a suitable choice of supercell size are computationally inexpensive alternatives to PBE0 for phonon analyses of defects in BaZrO$_3$.

Regardless of the approach, the calculated $\Delta S^{vib}$ is considerably more negative for $v_O^+$ than $v_O$, as expected from both the

![Fig. 4](image-url)  
**Fig. 4** Phonon density of states (PDOS) calculated for the $2 \times 2 \times 2$ (left) and $3 \times 3 \times 3$ (right) BaZrO$_3$ supercells. In each plot, the PDOS is reported for the perfect system (unfilled curve) and the defective systems containing the neutral oxygen vacancy $v_O$ (blue) and the double charged oxygen vacancy $v_O^+$ (red).
Fig. 5  Phonon contribution to the formation enthalpy (a and b) and entropy (c and d) of $v^+_0$ (a and c) and $v^+_0$ (b and d).

Fig. 6  (left) Vibrational contributions to the free formation energy ($\Delta G^{\text{vib}}$) of $v^+_0$ and $v^+_0$ in BaZrO$_3$ calculated using CRYSTAL/PBE0 and VASP/PBE in a $3 \times 3 \times 3$ supercell at standard pressure. (right) Formation energy ($\Delta G$) of oxygen vacancies as a function of the Fermi energy (eqn (1)) calculated using VASP/PBE in a $3 \times 3 \times 3$ supercell at $T = 0$ K and 1000 K.
greater local relaxations, and the more negative formation volume of the former. Therefore, the vibrational contribution to the Gibbs free energy ($\Delta G^{\text{ vib}}$) of formation is particularly relevant for $v^*$ at high temperatures. This is illustrated in Fig. 6, which shows $\Delta G^{\text{ vib}}$ of $v^*$ and $v^0$ calculated using CRYSTAL/PBE0 and VASP/PBE in a $3 \times 3 \times 3$ supercell at standard pressure. $\Delta G^{\text{ vib}}$ is slightly lower using VASP than using CRYSTAL for both defects due to the slightly more negative $\Delta S^{\text{ vib}}$ obtained using CRYSTAL. Further, due to the more negative $\Delta S^{\text{ vib}}$ of $v^*$ than $v^0$, the former becomes more unstable with respect to the latter with increasing temperature. As the relative stability of $v^*$ and $v^0$ determines the thermodynamic charge transition level of the oxygen vacancy, inclusion of phonons has a drastic effect on the transition level at $T > 0 \text{ K}$ (Fig. 6, right). At 0 K, the charge transition level occurs at 0.42 eV below the conduction band (with VASP/PBE), which is in good agreement with the results reported by Sundell et al.\textsuperscript{24} With the increase in temperature, $\Delta G$ of $v^*$ remains essentially constant due to the large negative $\Delta G^{\text{ vib}}$, which is counteracted by the entropy change due formation of $O_2(g)$. For $v^0$, however, the entropy change due to $O_2(g)$ formation is greater than $\Delta G^{\text{ vib}}$ and $\Delta G$ decreases significantly with increasing temperature. Hence, the charge transition level occurs at increasingly lower values with increasing temperature, and is at for instance 1000 K shifted to 0.83 eV below the conduction band minimum. As the effect of phonons on the thermodynamic properties of $v^*$ and $v^0$ stems from their different structural relaxations, this temperature effect on the charge transition level would only be observable using electrical techniques, and not by using optical techniques. It should however be noted that, even if lattice vibrations tend to favor neutral oxygen vacancies at high temperature, the configurational entropy term (as included indirectly using the mass action law) increases the stability of charged oxygen vacancies with respect to the neutral ones at high temperature, due to the larger number of possible configurations for the system $v^* + 2e^-$ as compared to $v^0$.

### 4. Conclusions

In this contribution, we studied the electronic and thermo-dynamic properties of neutral and charged oxygen vacancies in BaZrO$_3$ with emphasis on the contribution from phonons. For completeness, we employed two complementary DFT approaches; LCAO calculations using the CRYSTAL14 code with two different BSs (BS1 and BS2) and the hybrid PBE0 functional, and PAW calculations using VASP and the GGA-PBE and GGA-RPBE functionals. For defect-free BaZrO$_3$, both CRYSTAL/PBE0 and VASP/PBE or RPBE approaches estimate vibrational frequencies at the $\Gamma$-point in good agreement with the experimental values. The lowest frequency modes obtained at the R-point are, however, softer using VASP/PBE or RPBE, than using CRYSTAL, which affects the defect entropies calculated using supercells which sample the R-point.

Using CRYSTAL/PBE0, we found that $v^0$ induces a deep level in the band gap ($\approx 1.5 \text{ eV}$ from the conduction band bottom), while the underestimated band gap calculated using VASP/PBE predicts a defect level much closer to the conduction band.

The phonon calculations reveal that both vacancy charge states induce a new IR and Raman active lattice vibration at $\approx 650 \text{ cm}^{-1}$ that should be experimentally detectable. This is in line with recent observations for defective SrTiO$_3$\textsuperscript{64} and could therefore be a general feature of oxygen vacancies in perovskite-structured oxides. In general, both adopted approaches predict similar structural and thermodynamic properties of the defect in the two charge states. Furthermore, $v^*$ induces significantly larger structural distortions than $v^0$, and displays more negative formation volumes, which causes a noticeably blue shift of the phonon spectrum. Hence, while the contribution from phonons to the Gibbs free energy of formation is small for $v^0$ (0.1 eV at 1000 K), it is as large as 1 eV at 1000 K for $v^*$. Phonons therefore affect the relative stability of $v^0$ and $v^*$ as a function of temperature, resulting in a temperature-dependent charge transition level. By assuming temperature independent band edges, the charge transition level (+2/0) shifts from 0.42 to 0.83 eV (calculated using VASP/PBE) below the conduction band bottom from 0 to 1000 K (the real shift would however also be affected by changes in the band edges with temperature).

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### References
