

Electron-Phonon Renormalization in the Proton-Conducting Electrolyte BaZrO₃ and Its Implications for High-Temperature Electrolysis

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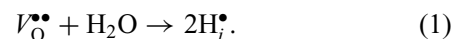
Electrical leakage is an inherent problem in solid-oxide fuel and electrolyzer cells, limiting their energy-conversion efficiency. High concentrations of electrons or holes can exacerbate this issue. However, it is largely unclear how the typical high operating temperatures of the systems influence their charge-carrier concentrations. In this work, we use first-principles calculations to examine how lattice vibrations impact electrical conductivity in conventional electrolytes, using BaZrO₃ as a representative material. Our analysis shows that phonon-induced shifts in the band gap and band edges lead to a dramatic increase in *p*-type carrier concentrations at temperatures above 600 K, compared to models that neglect temperature effects. Additionally, we reveal the importance of oxygen-ion motion on band-edge positions, which makes valence-band-edge shift dominate the band-gap change. Our study provides a protocol for calculating phonon-induced changes in similar oxides, paving the way for interrogating electrical leakage in electrolytes for high-temperature operation.

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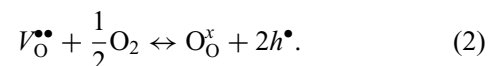
I. INTRODUCTION

Solid-oxide ionic conductors have broad applications in various energy-conversion technologies, such as electrolytes in solid-oxide fuel cells (SOFCs) and electrolyzer cells [SOECs; see Fig. 1(a)]. The ionic transport properties of those electrolytes play an important role in determining the overall energy-conversion efficiency of the devices. Proton-conducting oxides (PCOs) have attracted particular interest, as their operating temperatures are considerably lower than those of oxide-ion conductors [1,2]. Barium zirconate (BaZrO₃, BZO), barium cerate (BaCeO₃, BCO), and their alloys are among the most studied PCOs [3–5]. BZO-BCO alloys in particular provide both excellent chemical stability and high proton conductivity (about 0.01 S cm⁻¹ at 600°), which can be tuned through adjustments in the Ce:Zr ratio and the incorporation of dopants [6–10].

In addition to protons and oxide anions, other charge carriers such as electrons and holes may also drift in response to the chemical or electrical potential, giving rise to undesirable electrical leakage [11] [Fig. 1(b)]. Electrical leakage consumes input energy without contributing to the electrical-chemical conversion output and thus deteriorates the energy-conversion efficiency of the device [11]. It has been reported that the Faradaic efficiency of conventional PCOs is between 50% and 90% [12] and various strategies can be used to enhance the efficiency, as summarized by Gaikwad *et al.* [13]. For typical PCOs, oxygen vacancies ($V_{\text{O}}^{\bullet\bullet}$) are directly linked to the introduction of protons H_i^+ :



However, oxygen vacancies may also introduce holes under O₂-rich conditions through oxidation:



Thus, PCOs may experience intrinsic hole conduction, particularly where the air electrode in an SOFC or SOEC is exposed to high oxygen partial pressures (P_{O_2}). Several experimental studies have reported orders-of-magnitude changes in electrical conductivity in BZO [14,15] as a

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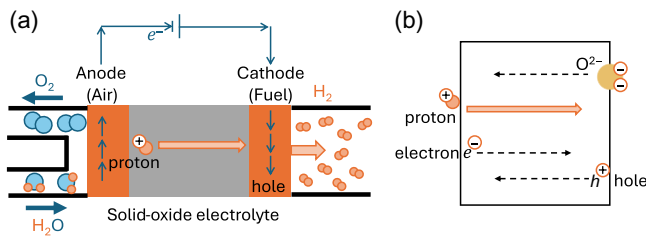


FIG. 1. (a) A schematic representation of a proton-conducting solid-oxide electrolyzer cell (p-SOEC). Water steam comes into the cell at the anode and oxygen is produced at the same electrode, while protons are transported to the cathode and generate hydrogen. (b) Possible charge carriers in proton-conducting oxides: protons, oxygen ions, electrons, and holes.

function of temperature, P_{O_2} , and water-vapor partial pressure ($P_{\text{H}_2\text{O}}$). Since electron (n -type) conductivity is low in BZO ($<10^{-10}$ S cm^{-1}) [7,16], holes are the main charge carriers that lead to such a dramatic change.

Hole conduction in BZO, however, is not well understood. As the conductivity is determined by both mobility and concentration, theoretical studies have sought to address both aspects. Equation (2) assumes p -type carriers to be delocalized band states, while Lindman *et al.* [17] and Rowberg *et al.* [18] have shown that the formation of hole polarons in the material is quite favorable, suggesting that they may dominate the leakage current.

On the other hand, the accurate calculation of hole concentrations depends strongly on the description of the density of states near band edges, defect formation energies (exponentially related to defect concentrations [19]), functional choice [20], and band-edge positions [21,22]. Due to the high operating temperature range of these electrochemical devices, temperature effects are particularly relevant. In fact, several studies have considered temperature effects on both vibrational and gas-phase contributions [19,20,23–25] to the defect formation energies in BZO. Specifically for vibrational contributions, local anharmonicity in the bonds surrounding the defects has also been investigated [26,27], as it may influence formation energies as the temperature increases. Nevertheless, the temperature dependence of the electronic structure, as influenced by the electron-phonon renormalization of the band gap, has mostly been overlooked when calculating defect formation energies. Relatively few studies have included the temperature dependence of the band edges [27,28] and the impact of these considerations on electrical leakage in PCOs has not been rigorously addressed.

Here, to address this knowledge gap, we use first-principles calculations to uncover the impact of phonons on electron-phonon renormalization of the band gap (simplified as band-gap renormalization in the following) and the resultant change in the charge-carrier concentration,

using BZO as a prototypical material. By carefully benchmarking computational parameters and levels of theory, we provide a robust band-gap-renormalization description with both harmonic and quasiharmonic approximations. We then discuss how the band-edge shift modifies electron and hole concentrations and discuss possible strategies to limit the electrical leakage. We also briefly discuss computational challenges in calculating the band-gap renormalization in BZO. Our study provides a protocol to compute the effect of phonons on charge-carrier concentrations in oxide electrolytes, paving a way to tackle the electrical-leakage issue.

II. RESULTS AND DISCUSSION

A. Electronic structure of ground state

To obtain the band-gap renormalization, we first calculate the band gap of the ground-state crystal structure and its associated phonon properties. Experimentally, BZO maintains the cubic perovskite structure close to 0 K [29]. In Fig. 2(a), we show the optimized cubic BZO structure. Some prior first-principles phonon calculations for BZO have suggested that the cubic phase is dynamically unstable at 0 K due to an imaginary phonon mode at the R phonon wave vector [30,31], which represents the rotation of ZrO_6 octahedra and indicates an antiferrodistortive transition from cubic to other crystal structures. However, this result is highly sensitive to the choice of exchange-correlation functional and pseudopotentials [29]. Here, we have computed the crystal structure of BZO, the electronic structures, and the phonon properties using two popular functionals. These include the generalized-gradient-approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE) [32,33] and the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [34,35], along with two types of pseudopotentials, based on the norm-conserving (NC) approach and projector augmented waves (PAWs). A detailed comparison and validation of our results against previous experimental and computational data sets are provided in Tables S1, S2, and S3 and Fig. S1 in the Supplemental Material [36]. While the HSE functional describes lattice parameters and the band gap more accurately, we have found the PBE functional with PAW-type pseudopotentials to be qualitatively correct, with the advantage of being computationally more affordable for band-gap-renormalization calculations. A summary of the impact of the computational parameters on band-gap renormalization and the justification of our choice can be found in Sec. II D.

As shown in Fig. 2(b), the phonon dispersion obtained from the PBE functional with PAW pseudopotentials is non-negative, indicating the stability of the cubic phase at 0 K. The calculated phonon frequencies are consistent with previous PBE results [31], although they are slightly lower than experimental values based on Raman spectra

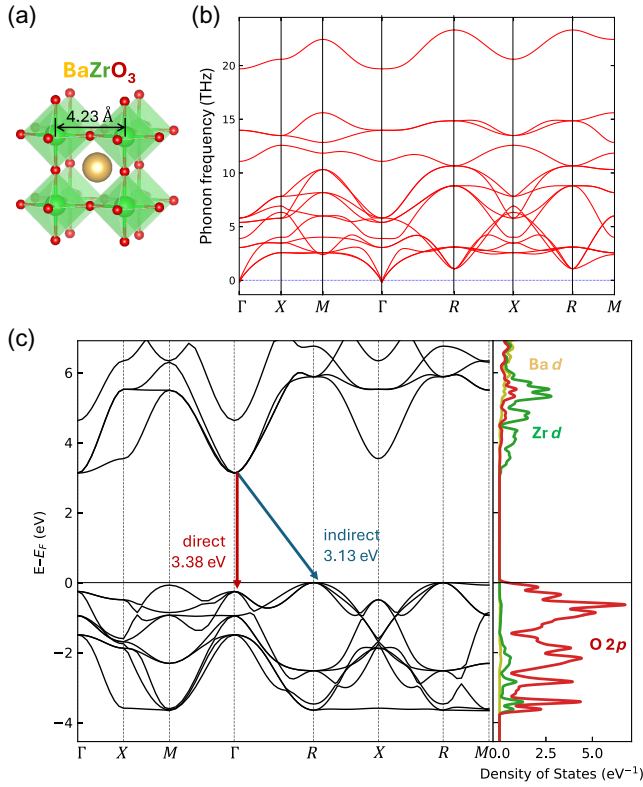


FIG. 2. The computed electronic structure and phonon properties of cubic BZO from density-functional theory (DFT) using the Perdew-Burke-Ernzerhof (PBE) functional with the projector augmented wave (PAW) pseudopotential. (a) The PBE-optimized lattice parameters of BZO. (b) The phonon dispersion relationship. (c) The electronic band structure and projected density of states of BZO.

[31] (approximately 0.6% lower; for a detailed comparison, see Table S3 in the Supplemental Material [36]). These smaller phonon frequencies, together with a slightly larger lattice parameter compared to experimental values [29,37] (approximately 0.6% higher; see Table S1 in the Supplemental Material [36]), are a consequence of the known tendency of the PBE functional to underestimate bond stiffness, which will also impact some thermodynamics properties of BZO, as we will discuss. We have also obtained the corresponding electronic band structure at the PBE level [Fig. 2(c)], showing an indirect band gap of 3.13 eV located between the Γ and R points and a direct band gap of 3.38 eV located at the Γ point, consistent with previous PBE results [38]. Those values are about 1.5 eV lower than experimental results [39–41] due to the well-known self-interaction error in standard GGA functionals. The band-gap renormalization we have obtained from this functional is thus likely to represent lower bounds for experimental measurements. From the projected density of states [Fig. 2(c)], it can be seen that the valence-band edge

is mainly composed of oxygen 2p orbitals, in agreement with previous calculations [18].

B. Electron-phonon renormalization of the band gap

We have then calculated the band-gap renormalization due to phonons, i.e., the band-gap difference between distorted and ground-state structures, and band-edge shifts as a function of temperature, as shown in Fig. 3. In general, three levels of theories have been considered to generate the distorted structures. First, we have employed the harmonic approximation, in which phonons are treated as harmonic vibrations and ion displacements to follow the phonon dispersion obtained for the ground-state structure. Second, we have utilized the quasiharmonic approximation (QHA) [42], in which the volume is taken as the second variable besides temperature in free-energy calculations. In this approach, the cell volume varies with the temperature and harmonic phonons are obtained for each volume to generate the distorted structures. Finally, we have considered the anharmonic treatment that accounts for phonon-phonon interactions, requiring the inclusion of third- and fourth-order force constants to generate the distorted structures [43,44]. Anharmonic effects are typically important for thermoelectric and ferroelectric materials [45], which is not the case for BZO. We have therefore primarily focused on the harmonic approximation and the QHA in our analysis.

Since numerous distorted configurations are possible at any temperature, we have used different strategies to effectively sample the configuration space. We have applied both the one-shot method developed by Zacharias and Giustino (the ZG method) [46] and the thermal-line sampling method [47,48] to ensure the convergence of band-gap change with respect to the supercell size, as shown in Fig. 3(a). A detailed discussion on supercell size convergence can be found in the Supplemental Material [36]. Overall, all results identify a significant band-gap decrease at elevated temperatures due to phonon effects. We have further included the QHA on top of the ZG method. First, to validate the QHA with the PBE functional and PAW pseudopotentials, we have compared several computed thermodynamic quantities of BZO to previous experimental and computational work. As summarized in Table I, we find good agreement between our calculations and experiments. Our computed thermal-expansion coefficient is particularly close to experimental measurements, indicating that the volume change used for our band-gap-renormalization calculations is reliable. We also note the slightly larger lattice constant at 300 K (approximately 0.9%, optimized by minimizing the QHA free energy) and the smaller bulk modulus obtained from the PBE functional compared to experimental values. Again, this discrepancy arises from the tendency of PBE to predict softer bonds, consistent with the findings of a previous study

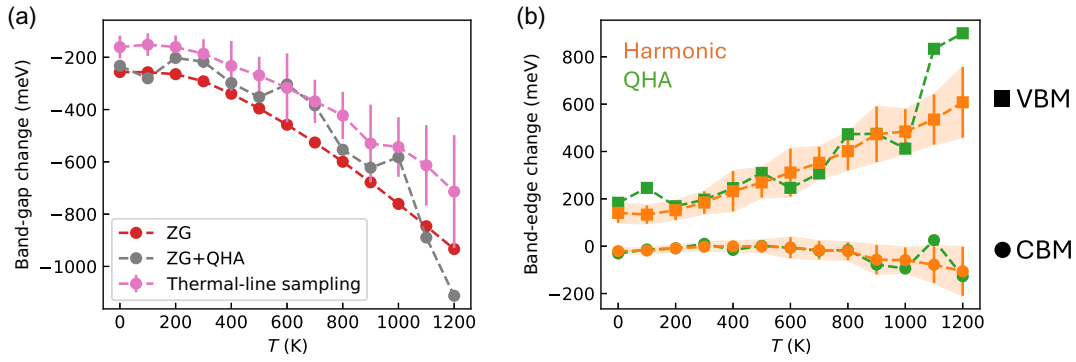


FIG. 3. The computed band-gap change and band-edge shift in BZO as a function of temperature using a $5 \times 5 \times 5$ supercell, with PBE+PAW. (a) The band-gap change obtained from the Zacharias-Giustino (ZG) one-shot method, the quasi-harmonic approximation (QHA) on top of the ZG method, and the thermal-line sampling method. The error bars for the thermal-line sampling method come from standard deviations of the band gap obtained from 200 sampled configurations. (b) The conduction-band minimum (CBM) and valence-band maximum (VBM) energy shifts with harmonic approximations (constant volume) and with QHA treatment on top of thermal-line sampling.

comparing the accuracy of various functionals for predicting vibrational properties [29]. We have then obtained ZG structures for each volume at the corresponding temperature and computed the band-gap change. As shown in gray in Fig. 3(a), the band-gap-renormalization change is less monotonic compared to the harmonic case at the fixed volume, likely due to two concurrent variations at different temperature conditions: (1) that the phonon dispersion changes with volume and (2) that the ZG configuration varies with volume. In general, though, the ZG+QHA method closely follows the non-QHA predictions, with values bounded by the ZG method and thermal-line sampling method, except for $T > 1000$ K, where the role of volume expansion is more critical. However, such temperatures exceed the typical operating range of BZO in SOFCs and SOECs [10].

The decrease of the band gap with phonons explicitly considered stems from the combined shifts of conduction- and valence-band edges. In Fig. 3(b), we show the band-edge shifts for both the conduction-band minimum (CBM) and the valence-band maximum (VBM), with and without the QHA (harmonic approximation), respectively. The band-edge shifts due to electron-phonon renormalization are defined as

$$\Delta E = E_{\text{VBM(CBM)}} - E_{\text{VBM(CBM)}_V}, \quad (3)$$

where VBM(CBM) refers to band edges in distorted structures generated from either the harmonic or the quasi-harmonic approximation, and VBM(CBM)_V refers to band edges in *nondistorted* structures at the corresponding cell volume. For the harmonic case, the nondistorted structure is simply the ground-state structure; for the QHA, it refers to volume-expanded structures without finite-temperature distortions. (We show how VBM(CBM)_V changes as a function of T in Fig. S5 in the Supplemental Material [36].)

In Fig. 3(b), we show that the ΔE values obtained from the harmonic and quasi-harmonic approximations are consistent for $T < 1100$ K, where the VBM shift dominates the band-gap change across the entire temperature regime. This is due to the valence-band edge being composed mainly of oxygen $2p$ orbitals [Fig. 2(c)]. As oxygen-ion vibrations account for most phonon modes and dominate at temperatures above 500 K [31], the valence-band edge should shift more significantly with increasing temperature than the conduction-band edge. We have indeed observed a more flattened valence-band edge with a larger energy shift in momentum space for distorted high-temperature structures, relative to the conduction-band edge (Fig. S2 in the Supplemental Material [36]).

Similar to the trend in band-gap change, the QHA leads to more fluctuations in the band-edge shifts compared to the harmonic case. However, the QHA data are generally within the statistical error bar obtained by thermal-line sampling within the harmonic approximation. This fluctuation can be due to two reasons: (1) thermal fluctuation of sampled structures and (2) the fact that the phonon frequencies slightly vary with volume expansion, as they have been calculated in each volume with the QHA. In Fig. 3(b), it is also shown that the QHA-calculated VBM shift is more significant than that from the harmonic case for $T > 1100$ K, indicating that the phonon spectra obtained at that volume expansion are drastically different than those in the ground-state structure.

C. Charge-carrier concentrations

Using our computed VBM and CBM offsets from Fig. 3(b), we have calculated the change in the charge-carrier concentrations in BZO as a function of temperature. To do so, we have first integrated over the calculated density of states using Fermi-Dirac statistics to determine the

TABLE I. Computed thermal properties of BZO using the QHA with the PBE functional and PAW pseudopotentials.

	This work	Experimental references	Computational references
Lattice constant (Å) at 300 K	4.232	4.192 (Ref. [49])	
Bulk modulus K_0 (GPa, room temperature)	149	189 (Ref. [50])	
Linear thermal-expansion coefficient (10^{-6} K^{-1} , above 1000 K)	7.67	7.13–7.84 (Refs. [50–52])	5.4 (Ref. [53]), 11.77 (Ref. [54])
Debye temperature (K)	500–600	544 (Ref. [50])	
Specific heat C_p (J/mol K)	123 at 1000 K, 107 at 300 K	120 (Ref. [50]) at 1000 K, 100 (Ref. [51]) at 300 K	127.6 (Ref. [55]) at 1000 K, 107 (Ref. [55]) at 300 K
Grüneisen parameter	1.32 at 500 K	1.398 at 500 K (Ref. [51])	

charge-carrier concentration as a function of the Fermi-level position. Subsequently, we have self-consistently calculated the position of the Fermi level assuming net charge neutrality among charge carriers, native defects, and impurities (e.g., yttrium dopants and hydrogen), mirroring our previous calculations from Ref. [19]. Here, however, the defect formation energies and carrier concentrations are shifted according to our computed band-edge offsets, allowing us to investigate the role of temperature.

Our results are shown in Fig. 4. We focus on conditions that are most relevant experimentally by interpolating between the chemical potentials of oxygen, hydrogen, and water at the fuel and air electrodes in a typical p-SOEC. Specifically, we assume $P_{\text{H}_2} = 1 \text{ atm}$ and $P_{\text{O}_2} = 7 \times 10^{-20} \text{ atm}$ at the fuel electrode, and $P_{\text{O}_2} = 0.7 \text{ atm}$ and $P_{\text{H}_2\text{O}} = 0.3 \text{ atm}$ at the air electrode, following our treatment in previous work [19]. We have also studied the carrier-concentration variation over a wider range of chemical conditions (see Fig. S6 in the Supplemental Material [36]). We first focus on holes [Fig. 4(a)] and electrons [Fig. 4(b)] and examine the impact of band-gap renormalization by comparing results without band-gap renormalization and with band-edge shifts at the QHA level. At both temperatures indicated (600 K and 900 K, representing the approximate limits of proton conduction in BZO), band-gap renormalization increases the hole concentrations by roughly 4 orders of magnitude, indicating that finite-temperature effects play a significant role. Depending on P_{O_2} and $P_{\text{H}_2\text{O}}$, a similar magnitude of increase in the electrical conductivity may lead to a decrease in the ionic transference number of more than 50%, corresponding to a sharp drop in the Faradaic efficiency [14]. The inclusion of the band-gap shift in BZO is therefore important for accurate evaluation of its Faradaic efficiency. Conversely, the electron concentrations decrease by about 2 orders of magnitude in the band-gap-renormalized system. This result shows that the upward shift of the VBM plays a more dominant role than the downward shift of the CBM in the defect and charge-carrier chemistry of BZO, as the overall effect is for the Fermi level to drop relative to the VBM.

In Fig. 4(c), we plot concentrations of all relevant species—protons, oxygen vacancies, holes, and electrons—as a function of temperature, focusing on conditions at the fuel and air electrodes separately. Concentrations for a wider range of conditions are also depicted in Fig. S7 in the Supplemental Material [36]. Unsurprisingly, at both electrodes, protons will dominate the defect chemistry, with oxygen vacancies overtaking them slightly at the fuel electrode approaching 900 K (close to temperatures at which oxide conductivity surpasses that of protons). We note that our predicted proton concentrations are consistent with experimental measurements: Han *et al.* [56] have reported a proton concentration at the air electrode for 20% Y-doped BZO of between 1.3 and $1.9 \times 10^{21} \text{ cm}^{-3}$, exceptionally close to our calculated concentration of $2.3 \times 10^{21} \text{ cm}^{-3}$ under similar conditions. However, the hole concentrations are fairly robust at both electrodes and they clearly overwhelm the electron concentrations, matching experimental findings that *p*-type electrical leakage is most relevant in BZO [16,57,58]. Holes will also be the most significant minority carrier at the air electrode, surpassing oxygen vacancies. In both cases, our results suggest that *p*-type electrical leakage should not be neglected. Furthermore, it will increase with temperature, in agreement with experimental measurements of electrical conductivity in BZO showing an increase of several orders of magnitude over a similar temperature range [15].

D. Impact of computational parameters

Finally, we briefly discuss how our choice of computational parameters impacts the band-gap renormalization and charge-carrier concentration change. An accurate band-gap renormalization depends on three components: (1) accurate band-gap results, (2) phonon properties, and (3) the correct description of electron-phonon coupling. We have found that the PBE functional with PAW pseudopotentials provides qualitatively correct results for the three parts, although it underestimates the band gap (approximately 32% lower) and slightly overestimates the phonon frequencies (approximately 0.6%).

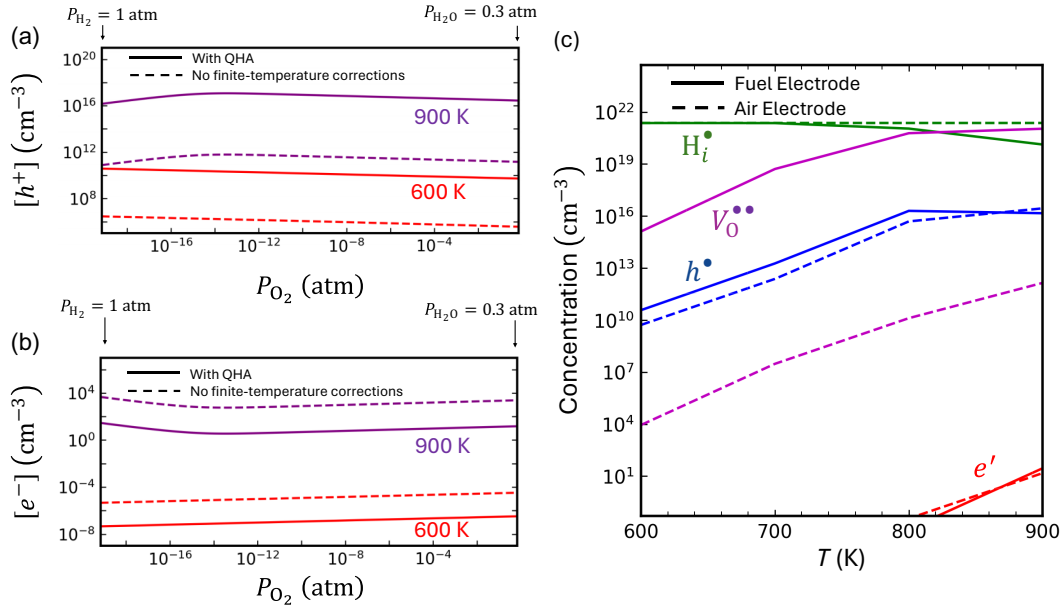


FIG. 4. The concentrations of (a) holes and (b) electrons as a function of the chemical potential. The conditions are set to vary between those of a typical fuel electrode (left; $P_{\text{H}_2} = 1$ atm) and air electrode (right; $P_{\text{O}_2} = 0.7$ atm, $P_{\text{H}_2\text{O}} = 0.3$ atm). The concentrations are shown for the band-renormalized case (solid lines) and the uncorrected case, assuming the 0-K band structure (dashed lines). Data for $T = 600$ K and 900 K are shown to capture the range of relevant conditions for proton conduction. (c) The concentrations of protons ($\text{H}_i^\bullet$), oxygen vacancies ($\text{V}_\text{O}^\bullet$), holes ($h^\bullet$), and electrons (e') at conditions corresponding to the fuel electrode (solid) and air electrode (dashed) as a function of temperature.

Our results for band-gap renormalization and charge-carrier concentration change are thus qualitatively correct in trend, but their actual magnitudes may be different. We have also found that the use of NC pseudopotentials leads to a negative phonon frequency at the R point (see Fig. S1 in the Supplemental Material [36]). However, this difference has a negligible impact on the calculated band-gap renormalization (see Fig. S3 in the Supplemental Material [36]). The HSE06 functional provides a quantitatively accurate description of the band-gap and phonon properties. However, due to the relatively large supercell required for distorted structures, the use of a hybrid functional may be computationally infeasible.

III. CONCLUSIONS

In summary, we have calculated the electron-phonon renormalization of the band gap in BaZrO_3 as a function of temperature to assess its impact on electronic carrier concentrations in BZO-based electrolytes at typical operating conditions in SOFCs and SOECs. The results have been computed from first principles using the PBE functional and PAW pseudopotentials, where we have considered both the purely harmonic approximation (neglecting volume changes) and the QHA (including volume changes) to treat electron-phonon interactions, which monotonically decrease the band gap by approximately 150–900 meV

between 0 K and 1200 K. Within both the harmonic and quasiharmonic approximations, the VBM shift accounts for most of the band-gap decrease. We have found carrier concentrations to be considerably larger when electron-phonon renormalization is considered, with hole concentrations increasing by about 4 orders of magnitude. Such an increase may lead to a sharp drop in the Faradaic efficiency under specific P_{O_2} and $P_{\text{H}_2\text{O}}$ conditions. We conclude that electron-phonon renormalization of the band gap plays an important role in accurately modeling the conduction mechanisms in solid oxides subject to high-temperature operating environments such as in SOECs and SOFCs, particularly in describing phenomena contributing to unwanted electrical leakage. Future work providing experimental validation for our calculated band-gap change as a function of temperature in BZO will be valuable, as will the extension of our current computational framework to other BZO- and BCO-based electrolytes.

IV. METHODS

As shown in Fig. 5, the general procedure for our electron-phonon renormalization calculations is as follows: (1) obtain the band gap of the ground-state structure; (2) calculate the phonon dispersion; (3) obtain distorted structures according to phonon modes; and (4) calculate the band gaps of distorted structures and compare to the

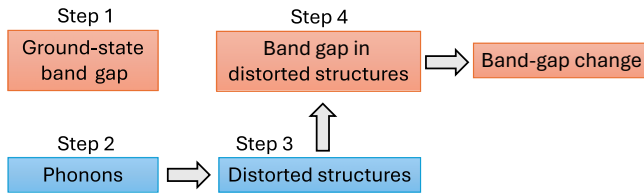


FIG. 5. The general procedure to calculate electron-phonon renormalization of the band gap. For the step 2 phonon calculations, different theory levels exist, from harmonic approximation to the QHA and to anharmonic effects. For step 3, various sampling methods, such as the ZG one-shot method, have been developed to obtain representative distorted structures.

value obtained in step 1. The band gap and other electronic structure properties of the ground-state and distorted structures have been calculated using density-functional theory (DFT) as implemented in the QUANTUM ESPRESSO (QE) code, v7.2 [59–61]. We have tested the PBE [32] and HSE06 functionals [62]. Both the PAW pseudopotential (pp) [63] and the NC pp [64] from Pseudo Dojo [65] have been tested for the PBE functional (PAW JTH v1.1 and NC-sr-v0.5), where the Ba $5s^2 5p^6 6s^2$, Zr $4s^2 4p^6 5s^2 4d^2$, and O $2s^2 2p^4$ electrons are treated explicitly as valence. Only the NC pp has been used for the HSE06 functional. For the PAW pp, the energy cutoffs for the wave functions and the charge density were 75 Ry and 300 Ry, respectively, and for the NC pp, they were 80 Ry and 320 Ry, respectively. Monkhorst-Pack k -point sampling with an accuracy of $0.0397 \text{ \AA}^{-1}$ ($6 \times 6 \times 6$ for the primitive five-atom BZO cell) has been used. The band-structure unfolding for distorted supercells has been obtained using BANDS_UNFOLD.X implemented in QE.

Phonon calculations using the finite-displacement method and thermal properties using the quasiharmonic approximation have been carried out using the PHONOPY code [66,67] in conjunction with QE (to obtain interatomic forces). A $3 \times 3 \times 3$ BZO supercell size has been used to converge the phonon dispersion and a $5 \times 5 \times 5$ supercell size has been used to obtain the phonon dispersion for the band-gap-renormalization calculations. Nonanalytic corrections have been applied, with the dielectric constant and effective Born charge obtained from density-functional perturbation theory (DFPT), implemented in QE. To sample distorted structures, we have used the ZG [46] and thermal-line sampling methods [47], implemented in the PyEPFD code [68,69], which can read force-constant files obtained from PHONOPY.

The concentrations of electrons and holes have been determined as a function of the Fermi-level position by integrating the calculated density of states near the band edges [70]. Subsequently, the Fermi level corresponding to charge neutrality between defects, impurities, and charge carriers has been determined iteratively using previously

calculated defect formation energies [18,19,71]. Using the well-established formalism for calculating charged defect formation energies [72], and following the approach laid out in our previous work [19], the defect formation energies have been calculated assuming intermediate chemical potentials between the Ba-rich and Zr-rich limits for the thermodynamic stability of BZO, and a fixed concentration of 20 at% yttrium has been assumed at the Zr site. Finite-temperature impacts on the formation energies have been considered implicitly for oxygen- and hydrogen-related species through the chemical potential, defined (in the case of oxygen) as

$$\mu_{\text{O}} = \frac{1}{2}E(\text{O}_2) + \Delta\mu_{\text{O}}, \quad (4)$$

where $E(\text{O}_2)$ is the total energy of an oxygen molecule calculated using DFT and $\Delta\mu_{\text{O}}$ captures deviations in the chemical potential due to the finite-temperature and pressure effects, as follows:

$$\Delta\mu_{\text{A}} = H^0(T) - TS^0(T) + RT \ln \frac{P_{\text{A}}}{P^0}. \quad (5)$$

Here, $H^0(T)$ and $S^0(T)$ are tabulated for O₂, H₂, and H₂O [73]; P_{A} is the partial pressure; and P^0 is the pressure at the standard conditions used in the tabulation. As far as solid reference phases are concerned (e.g., for Y, Ba, and Zr), finite-temperature effects are generally small and tend to cancel out when computing formation energies [72]; therefore, we neglect temperature effects for solid reference phases. We also include corrections to the formation energies of oxygen vacancies and interstitial protons due to temperature-dependent lattice vibrations, following the procedure outlined by Sundell *et al.* for oxygen vacancies [23] and Björketun *et al.* for protons [74]. We do not consider the impact of lattice thermal expansion on defect formation energies, as this effect is likely to be small on account of the small thermal expansion exhibited by BZO at the temperatures of interest [75].

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DATA AVAILABILITY

The data that support the findings of this paper are not publicly available. The data are available from the authors upon reasonable request.

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