Investigating Electronic, Optical, and Phononic Properties of Bulk $\gamma$-M$_2$ON$_2$ and $\beta$-M$_2$O$_8$N$_4$ (M = Hf and Zr) Insulators Using Density Functional Theory

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ABSTRACT: Hafnium and zirconium oxynitrides have similar properties, yet a consolidated investigation of their intrinsic properties has not been carried out. In this paper, we perform first-principles density functional theory calculations of $\gamma$- and $\beta$-phase hafnium and zirconium oxynitrides, which show that the $\gamma$-M$_2$ON$_2$ (M = Hf and Zr) is an indirect band gap ($E_g$) insulator, while the $\beta$-M$_2$O$_8$N$_4$ has a "pseudo-direct" type of $E_g$. The $\beta$-phase has higher $E_g$ than $\gamma$-phase, with concomitant disappearance of the conduction band tail. Optical properties in $\gamma$-M$_2$ON$_2$ show that the anisotropy is negligible, and the optical constant values are in the range of other superhard materials. Phonon calculations present peculiar characteristics such as a small phonon band gap in $\gamma$-Hf$_2$ON$_2$ and imaginary phonon frequencies in $\beta$-phases relating to lattice instability. The phononic properties are unfavorable for their potential use as an absorber material of the hot carrier solar cell—an emerging photovoltaic concept.

1. INTRODUCTION

Hafnium and zirconium oxynitrides are an interesting class of materials having applications in diverse areas such as renewable energy generation, semiconductor devices, corrosion-resistance coating, and temperature sensors, as discussed below. They are characterized by excellent hardness and exhibit polymorphism such that the proportion of O and N in the material can vary depending upon the growth conditions. Since O is more electronegative than N while N is more polarizable than O, the optical properties and electronic band-gap ($E_g$) values can be tuned.

Hafnium oxynitrides in the form of RHfO$_2$N perovskites (R = rare earth metals such as La, Nd, and Sm) and ZrO$_2$N$_y$ are promising photocatalytic materials for water splitting as they have a higher $E_g$ than the minimum threshold (1.23 eV) and good photocorrosion resistance. Photocatalytic water splitting is a clean energy harvesting technique in which H$_2$ from water is extracted, exploiting suitable $E_g$ and appropriate band offset values (with respect to water’s reduction and oxidation potentials) of semiconductors driven by photo-illumination. Ultrathin HfO$_2$N thin film is an active research material for high-k dielectric material in metal-insulator—semiconductor (MIS) devices, owing to high dielectric constant, low equivalent oxide thickness (EOT), and low leakage current. Further, HfO$_2$N is also a promising “solid electrolyte” in electrochemical metallization memory, a type of resistive random access memory (RRAM) devices based on the metal—insulator—metal (MIM) architecture. The application of both of these oxynitrides extends to temperature sensing devices due to excellent temperature sensitivity and thermal stability. Recently, a preliminary assessment indicated that HfO$_2$N$_y$ can have potential application in a hot carrier solar cell (HCSC). A HCSC is a so-called third-generation photovoltaic (PV) concept, which can, in principle, generate PV power with an efficiency of up to 66% in 1 sun. Despite multiple potential applications, there has been a limited theoretical study on these materials that explores electronic properties and no study regarding the optical and phononic properties to the best of our knowledge. In this paper, electronic, optical, and phononic properties of $\gamma$-M$_2$ON$_2$ and $\beta$-M$_2$O$_8$N$_4$ (M = Hf or Zr) phases are studied using the density functional theory (DFT) method and the results are consolidated in these isostructural compounds for the first time.

2. CRYSTAL STRUCTURE

Zirconium oxynitrides exist in many different phases such as $\gamma$-Zr$_2$ON$_2$, $\beta$-Zr$_2$O$_8$N$_4$, and $\beta$-Zr$_7$O$_{11}$N$_2$ with increasing O quantities in these polymorphs, respectively. The Hf counterparts are isostructural, owing to the very similar atomic...
radii of Hf$^{4+}$ and Zr$^{4+}$ and their position in the same group (IVB) of the periodic table.\(^5,8\) X-ray and neutron diffraction techniques suggested that the crystal structure of $\gamma$-Zr$_2$ON$_2$ is cubic bixbyite type.\(^17,20\) Examples of the bixbyite-type structures are c-$\text{V}_2\text{O}_5$, c-$\text{Ce}_2\text{O}_5$, and c-La$_2\text{O}_6$, which are body-centered cubic with space group $Ia\overline{3}$ [206]. Because the difference is so subtle, it is not trivial to distinguish if Zr$_2$ON$_2$ crystallizes in $Ia\overline{3}$ [206] or $Ibca$ [73] (a body-centered orthorhombic structure). Nevertheless, it was concluded that the N and O anions in the crystal are statistically disordered,\(^17,20\) and the structure is normally modeled with space group $Ibca$. The structure of $\beta$-Zr$_7$O$_8$N$_4$ was determined to be R3 from powder XRD techniques and is described as rhombohedrally distorted fluorite type.\(^6\) The $\beta$-Zr$_7$O$_8$N$_4$ is similar to $\beta$-Zr$_2$O$_3$N$_4$ (sometimes commonly called the “$\beta$” family) and belongs to the same space group R3 but has lattice parameter $c$ almost double that of the latter.\(^16\) In this work, $\beta$-M$_2$O$_1$N$_2$ is not investigated because of the uncertainty in the positions of N and O atoms in the unit cell.\(^21\) Based on X-ray diffraction, the $\beta$-family are referred to as “pseudo-cubic” due to their resemblance with cubic HfO$_2$.\(^2\)

The crystal structures of $\gamma$-M$_2$ON$_2$ and $\beta$-M$_2$O$_4$N$_4$ and the local environments are shown in Figure 1. In $\gamma$-M$_2$ON$_2$, the M$^{4+}$ cation is coordinated by 4 N and 2 O anions forming a highly distorted octahedron. The building blocks of the $\beta$-M$_2$O$_1$N$_2$ are the so-called “Bevan clusters”, designated as A$_6$X$_{12}$, and are obtained from a slight modification of the Zr$_7$O$_{14}$ unit—a building block of the cubic zirconia.\(^16,22\) In this environment, the central metal cation is 6-fold-coordinated by the anions, while the remaining cations are 7-fold-coordinated by the nearest anions, as shown in Figure 1d. The Brillouin zones (BZs) of the simulated crystal structures are drawn and shown in Figure S1.

### 3. COMPUTATIONAL DETAILS

The calculations were performed in the Quantum Espresso package,\(^23\) wherein generalized gradient approximation (GGA) exchange–correlation functionals parameterized with the Perdew–Burke–Ernzerhof (PBE) method\(^24\) were used along with the projector-augmented wave (PAW) pseudopotentials.\(^25\) The following were taken as the valence electrons for the calculations: (1) Hf: 5s$^2$6s$^2$5p$^6$5d$^2$, (2) Zr: 4s$^2$5s$^2$4p$^6$4d$^2$, (3) O: 2s$^2$2p$^4$, and (4) N: 2s$^2$2p$^3$. The BZ sampling was performed based on the Monkhorst–Pack $k$ and $\mathbf{q}$-point grid.\(^26\) The phonon frequencies were calculated based on the density-functional perturbation theory (DFPT).\(^27\) A very small self-consistency threshold (10$^{-14}$ Ry) was used for the sensitive phonon calculations.

For both electronic and phononic calculations in $\gamma$-Hf$_2$ON$_2$ ($\gamma$-Zr$_2$ON$_2$), the energy cutoff ($E_{\text{cut}}$) and the charge density cutoff ($\rho_{\text{cut}}$) values were 90 Ry (80 Ry) and 1080 Ry (960 Ry), respectively. A large value of $\rho_{\text{cut}}$ (12 times $E_{\text{cut}}$) was used to make sure that there is very little error in the phonon calculation. A $6 \times 6 \times 6$ $k$-point mesh was used for the electronic band calculations, while $2 \times 2 \times 2$ $q$-mesh (corresponding to 5 $q$ points) was used for calculating normal phonon modes in the phonon band calculations.

For the $\beta$-M$_2$O$_4$N$_4$ system, an $E_{\text{cut}}$ of 70 Ry, a $\rho_{\text{cut}}$ of 840 Ry, and a $k$-point mesh of $3 \times 3 \times 3$ were used. The phonon calculation was performed at 14 $q$ points in $\beta$-Hf$_2$O$_4$N$_4$ (corresponding to a $3 \times 3 \times 3$ $q$-point grid). The same was performed at 8 $q$ points only (corresponding to the $2 \times 2 \times 2$ $q$-point grid) in $\beta$-Zr$_7$O$_8$N$_4$ to save the computing resources. This did not reduce the quality and reliability of the results, as will be seen later in Section 4.3. The $E_{\text{cut}}$ and $k$-point values were finalized after a convergence test in each calculation. A description of the convergence test is provided in Figure S2, in which an $E_{\text{cut}}$ of $\gamma$-Zr$_2$ON$_2$ is shown as an example.

There were eight formula units of $\gamma$-M$_2$ON$_2$ (40 atoms) in the simulated conventional unit cell. The metal atoms occupied 8a, 8c, 8d, and 8e, while the anions occupied 16f Wyckoff positions of $Ibca$. The starting atomic positions were adopted from Bredow and Lerch,\(^28\) which were subsequently optimized for the final calculations. For $\beta$-M$_2$O$_4$N$_4$, three formula units (57 atoms) were simulated within the conventional unit cell. Starting atomic positions were taken from Bredow and Lerch\(^23\) for simulating in $P1$ (triclinic) setting. The coordinates and the path of the high-symmetry points in the BZ were taken from Setyawan and Curtarolo.\(^35\)

### 4. RESULTS AND DISCUSSION

#### 4.1. Crystallographic and Electronic Properties

Some crystallographic and electronic data are listed in Table 1. The lattice constant values from our work match well with other theoretical and experimental works. The $E_{\text{f}}$ value for $\gamma$-Hf$_2$ON$_2$ ($\gamma$-Zr$_2$ON$_2$) is 2.12 eV (1.66 eV). We also performed the calculations, allowing for the spin–orbit coupling (SOC) in both Zr and Hf compounds in the $\gamma$-phase. The results are presented in Note S1 and Table S1, which show that the fully relaxed lattice is undistorted when SOC is introduced as compared to the slightly distorted structures without the SOC.
Table 1. Crystallographic and Electronic Data of Hf and Zr Oxynitrides$^{a}$

|                | $\gamma$-Zr$_2$ON$_2$ | $\beta$-Zr$_2$O$_3$N$_4$ | $\gamma$-Hf$_2$ON$_2$ | $\beta$-Hf$_2$O$_3$N$_4$ |
|----------------|------------------------|--------------------------|------------------------|--------------------------|
| lattice        | cubic bixbyite (modeled as Ibca [73]) | rhombohedral, R3 [148] (modeled as triclinic P1) | cubic bixbyite (modeled as Ibca [73]) | rhombohedral, R3 [148] (modeled as triclinic P1) |
| lattice parameter (Å) | $a$: 10.136$^{d}$, 10.141, 10.125$^{f}$, 10.175$^{e}$, 10.220$^{k}$ | 9.625$^{d}$, 9.540$^{g}$, 9.540$^{i}$, 9.570$^{h}$, 9.538$^{k}$ | 9.972$^{b,d}$, 10.069, 9.880$^{d}$ | 9.481$^{d}$ |
|                | $b$: 10.197$^{d}$ | 9.574$^{d}$ | 10.033$^{b,d}$ | 9.409$^{d}$ |
|                | $c$: 10.199$^{d}$ | 8.919$^{d}$, 8.846$^{e}$, 8.846$^{i}$, 8.880$^{k}$, 8.850$^{k}$ | 10.026$^{b,d}$ | 8.787$^{d}$ |
| electronic band gap (eV) | 1.66$^{d}$, 2.50$^{e}$, 1.50, 1.9$^{d}$, 2.6$^{d}$ | 2.87$^{d}$, 4.4$^{b}$ | 2.12$^{d}$, 1.91$^{h}$, 2.83$^{i}$ | 3.36$^{d}$, 3.66$^{d}$ |
| direct band gap at $\Gamma$ (eV) | 1.77$^{d}$ | 2.90$^{d}$ | 2.24$^{d}$ | 3.40$^{d}$ |

$^{a}$The first-row values on each parameter (with superscript $d$) are from the current study (DFT). $^{b}$DFT calculation of the current work shows that the $\gamma$ phases are marginally different for $a$, $b$, and $c$. Although the crystal is cubic bixbyite, it is in line with the choice of the orthorhombic Ibca space group. $^{c}$Current work shows that the symmetry of $\beta$ phases is slightly lower than for the hexagonal axes setting of the trigonal Bravais lattice, which is consistent with the choice of the P1 (triclinic) system for the calculation. However, $b$ is marginally smaller than $a$. Note that this crystal system is also regarded as “pseudo-cubic” in the literature, as mentioned in the main text. $^{d}$Reference 15 (experimental). $^{e}$References 3, 17 (experimental). $^{f}$References 4, 20 (DFT). $^{g}$Reference 30 (DFT). $^{h}$Reference 7 (*) refers to DFT, ** refers to experimental. $^{i}$Reference 16 (experimental). $^{j}$Reference 22 (*) refers to DFT, ** refers to experimental. $^{k}$Reference 2 (experimental).

Figure 2. Electronic band dispersion. (a–d) $\gamma$-Hf$_2$ON$_2$, $\gamma$-Zr$_2$ON$_2$, $\beta$-Hf$_2$O$_3$N$_4$, and $\beta$-Zr$_2$O$_3$N$_4$ respectively. The right-hand side of each plot corresponds to the partial density of states.
The $E_g$ value is also slightly reduced with SOC. We leave the further investigation of the SOC effect for future studies. The $E_g$ values are underestimates compared to the experimental values, which is a common characteristic in a standard DFT method but are in good agreement with the values reported in the referenced theoretical work. A closer to the experimental, but higher than the current band-gap values of $\gamma$-Zr$_2$O$_7$ and $\beta$-Zr$_7$O$_8$N$_4$ is attributed to the implementation of a hybrid DFT method in the referenced works. The same hybrid functionals predicted better intrinsic properties for some oxides than the other exchange–correlation methods such as PBE, the one that is employed here. In Section 4.2, it will be seen that the calculated $E_g$ values are matching with the optical characteristics; however, due to the implementation of the PBE functionals, the values may be underestimated. For much precise band-gap and optical values, hybrid functionals or Hubbard-corrected DFT (DFT + $U$) methods can be tested. In this work, the focus is given to perform consolidated and simplified calculations and compare the properties among $\gamma$- and $\beta$-phases of the Hf and Zr counterparts; therefore, the choice of a certain type of exchange–correlation functional is noncritical.

The $\beta$-phases are more insulating than their corresponding $\gamma$-counterparts. This is intuitive because the oxynitride systems are related to the mixture of MO$_2$ and M$_3$N$_4$ in which the oxide phase has a higher $E_g$ than the nitride phase and if the O (N) proportion is maintained, $E_g$ of the oxynitride will increase (decrease). O in the $\beta$-phase is 42.11%, which is more than double the $\gamma$-phase (20%); hence, it has higher $E_g$. An interesting observation is that the indirect $E_g$ values in the $\beta$-phases are ~1% away from the direct gap at the $\Gamma$ point. Therefore, the band gap is a “pseudo-direct” type in the $\beta$-phase. On the other hand, the difference is greater than 5% in the $\gamma$-phase, so they are classed as having indirect $E_g$.

Figure 2 shows the calculated electronic band dispersion and partial electronic density of states (DOS) of both types of oxynitrides. The $E_g$ is indirect in all oxynitrides. The partial DOS of the isostructural oxynitrides are similar to each other; however, there are differences between the $\beta$- and $\gamma$-phases. In $\gamma$-M$_3$O$_7$N$_4$ (Figure 2a,b), the top of the valence band (VB) is primarily due to the N p-orbitals (red curves), while the O p-states (blue curves) occupy rather deeper levels and are strongly hybridized with the metal d-states. In $\beta$-M$_3$O$_7$N$_4$ (Figure 2c,d), the N p-orbital contribution shrinks as we move below the VB maximum, which is accompanied by a simultaneous increase in the O p-states. A strong hybridization of the N and O p-states near the VB maximum can be seen in all phases, while the conduction band (CB) minimum and higher states are mainly due to these M d-states. A distinguishing feature in the CB can be seen between the $\gamma$- and $\beta$-phases. In the $\gamma$-phase, a CB tail can be seen, which is completely absent in the $\beta$-phase, therefore widening the band gap. This may be related to the reduction in the Hf or Zr atomic proportion, from 40% in the $\gamma$-phase to 36.8% in the $\beta$-phase. We assume that the presence of more metallic cations in the $\gamma$-phase (as compared to the $\beta$-phase) lowers the band gap with the occurrence of the CB tail, which is similar to, for example, that in Cu$_2$ZnSnS$_4$ (CZTS) solar cell where Sn-rich composition shows a band-gap shrinkage with a band tail.

In all phases, N and O electronic contributions in the CBs are marginal but exhibit an interesting feature: in the $\gamma$-phases, the contribution due to the N p-states is almost double that of the O p-states (this is comparable to the atomic contribution of N (21.1%) and O (40%); however, there is no substantial difference in the $\beta$-phases although N (21.1%) is almost half of the O (42.1%). The effect of the s-orbitals on the electronic band diagram is not significant except in the very deep VB region where the majority of the dispersion is due to the N s-states (see Figure S3).

The observation that the N electronic states dominate over the O states near the VB maximum in all of these oxynitrides can be attributed to the larger number of partially filled 2p-states in N than in O. (There are three unpaired 2p-states in N and two unpaired 2p-states in O per atom.) However, in the $\beta$-phase, which has almost double the O-to-N atomic proportion as compared to the $\gamma$-phase, the higher O electronegativity should have an effect, which causes the O states to be closer to the core (nucleus) than the N states.
The isosurfaces of Kohn–Sham orbitals at the VB maximum (equivalent to the HOMO in molecular systems) and the CB minimum (equivalent to LUMO in molecular systems) can be visualized in Figure 3, which combines the directional information extracted from the reciprocal space to the DOS in Figure 2. The diagrams are for the hafnium compounds, but their zirconium counterparts have the same characteristics and are presented in Figure S4. These density contour maps are consistent with the discussion in the previous paragraph and with the DOS of Figure 2. For the VB maximum (Figure 3a,c), the p-orbital electrons are concentrated around the N and O atoms (see the purple dipole-shaped isosurfaces around blue N and red O atoms). The size of the dipole is bigger around the N atoms, which is consistent with the higher partial DOS at the VB maximum in Figure 2. In the CB minimum (Figure 3b,d), metal d-states are dominant (see the purple quadrupoles around the green metal atoms). Small-sized N and O 2p-states are also visible in the CB minimum. The size of the N p-orbital is bigger than the O p-orbital in the γ-phase (Figure 3b), while they are similar in the β-phase (Figure 3d); this is consistent with the partial DOS in the CB, as shown in Figure 2. Another peculiar characteristic can be seen around the metal cation in the CB minimum (Figure 3b,d). The isosurfaces around the metal look more symmetric and ordered in the γ-phase as compared to those in the β-phase, where the charge density shapes seem distorted. We attribute this to having two dissimilar metal cations along the c-axis of the Bevan cluster for which one cation (at the center of the Bevan cluster) is coordinated by six and the other is coordinated by seven anions, as described in Section 2 and Figure 1d.

4.2. Optical Properties. In this paper, optical properties are calculated for the γ-phases only. All other computational methods were similar except the choice of pseudopotentials in the optical property calculation where optimized norm-conserving Vanderbilt pseudopotentials have been used. The calculations were performed on 2744 equally weighted k-points generated by a 14×14×14 Monkhorst–Pack k-grid in the first BZ.

The material’s response to electromagnetic radiation is described by the frequency-dependent dielectric function \( \varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega) \). (The bracketed omega (\( \omega \)) will be avoided for simplicity from now on wherever possible.) This governs the propagation of light in a material, and many other micro-to macroproperties such as refractive index (\( n \)), absorption coefficient (\( \alpha \)), reflectivity (\( R \)), and transmittance depend on this. The imaginary part (\( \varepsilon_i \)) of the dielectric function characterizes the absorption of light and can be readily obtained from the electronic structure calculation, while the real part (\( \varepsilon_r \)) is obtained from the Kramers–Kronig transformation. All other optical properties can then be obtained from simple relations based on the dielectric functions. The following set of equations show the relations for \( n \), \( k \), \( \alpha \), and \( R \):

\[
n = \left[ \frac{\varepsilon_r}{2} + \sqrt{\frac{\varepsilon_r^2 + \varepsilon_i^2}{2}} \right]^{1/2}
\]
\[
k = \left[ -\frac{\varepsilon_x}{2} + \sqrt{\frac{\varepsilon_x^2 + \varepsilon_y}{2}} \right]^{1/2}
\]

(2)

\[
\alpha = \frac{4\pi k}{\lambda}
\]

(3)

\[
R = \frac{(1 - n)^2 + k^2}{(1 + n)^2 + k^2}
\]

(4)

Although \( \alpha \) and \( R \) are dependent on the fundamental optical values, they were calculated and presented in this study because these are the properties that are conveniently measured in labs and hence it will facilitate a direct comparison.

Figure 4 shows \( \epsilon_x, \epsilon_y \) and the electron energy loss function (ELF) of \( \gamma\)\text{-Zr}_2\text{ON}_2. The energy edge of \( \epsilon_x \) matches very well with the calculated \( E_g \) in both compounds. In the \( \epsilon_x \) spectra, only one principal peak can be seen at \( \sim 3.3 \) eV (\( \sim 2.8 \) eV) in \( \gamma\)\text{-Hf}_2\text{ON}_2 (\( \gamma\)\text{-Zr}_2\text{ON}_2), which is close to the corresponding \( E_g \) value. Therefore, these peaks can be assigned to the transition of valence electrons from mainly N 2p to metal d-states in the high-symmetry points of the first BZ. Because the \( \gamma\)\text{-M}_2\text{ON}_2 crystal deviates slightly from an ideal cubic system, the dielectric constant has different \( x, y, \) and \( z \) components, parallel to \( a, b, \) and \( c \) axes, respectively. The anisotropy related to this can be evaluated by calculating a ratio called the “static optical anisotropy” \( A_{\text{opt}} \) using eq 5

\[
A_{\text{opt}} = \frac{\epsilon_{\text{d}}(0)}{\epsilon_{\text{poly}}(0)} \left[ \frac{n_{\text{d}}(0)}{n_{\text{poly}}(0)} \right]
\]

(5)

where the subscript “d” refers to directions \( x, y, \) or \( z \) axes and the superscript “poly” refers to the “polycrystalline” static dielectric constant and refractive index, which can be calculated with the following equation

\[
\epsilon_{\text{poly}} = \left( \frac{\varepsilon_x^2 + \varepsilon_y^2 + \varepsilon_z^2}{3} \right)^{1/2}
\]

(6)

where the dielectric constant variable \( \varepsilon_x \) should be changed to \( n \) for the polycrystalline refractive index.

The optical anisotropy \( A_{\text{opt}} \), static dielectric constant \( -\varepsilon_x(0) \), and static refractive index \( n(0) \) values are presented in Table 2. A value of \( A_{\text{opt}} = 1 \) indicates a completely cubic system, which is isotropic. With increased anisotropy, this value diverges away from 1. It is clear from Table 2 that the \( \gamma \)-phases are almost isotropic, which is indeed consistent with their being represented by the cubic bixbyite type, as mentioned in Section 2. The static optical values are higher for \( \gamma\)\text{-Zr}_2\text{ON}_2 than for \( \gamma\)\text{-Hf}_2\text{ON}_2, which is consistent with its inverse relationship with \( E_g \). These values are slightly smaller than the purely semiconducting nitrides (\( \varepsilon_\text{M}(\text{N}_2) \)) \(^{37,38}\) and are comparable to the family of superhard spinel nitrides \(^{39,40}\) indicating why these oxynitrides have excellent hardness.

Figure 5 shows \( n, \alpha, \) and \( R \) of these compounds. Refractive index quite naturally follows a similar trend to \( \epsilon_x \) as shown in Figure 4. From the maximum value of 3.63 (at 3.35 eV) and 3.97 (at 2.84 eV) for \( \gamma\)\text{-Hf}_2\text{ON}_2 and \( \gamma\)\text{-Zr}_2\text{ON}_2, respectively, in the \( c \)-direction, the refractive index falls sharply on either side of the energy spectra. (The trend is similar in the \( a \) and \( b \) directions with a marginal difference in the peak position.) This includes a continuous reduction in \( n \) in the visible to infrared spectra until it saturates for the static values in \( \gamma \)-Hf oxynitride. The static refractive index value of \( \gamma\)\text{-Hf}_2\text{ON}_2 matches well with the experimentally measured value. \(^{41}\) Again, the absorption edge in the \( \alpha \) spectra is consistent with the respective \( E_g \) values and increases continuously until an absorption maximum is reached at an energy slightly higher than 10 eV for both materials. The locations of these maximum absorption peaks match with the maximum reflectivity, suggesting that around these energies, there will be very little photon transmission.

There is an important relation between the ELF and the \( R \) spectra. The prominent peak in ELF, which defines the screened plasma frequency \( \omega_p \) of the material, is accompanied by the trailing edge in the reflectivity curve. \(^{34,36}\) This is clearly observable in Figures 4 and 5 (the third-row subplots in each figure). In Figure S5, \( n, \alpha, \) and \( R \) are reproduced and presented as a function of wavelength in a typical UV–vis–NIR region so that they are easily comparable with experimental data when required.

4.3. Phononic Properties. The phonon dispersions are presented in Figure 6. For full dispersion, please see Figure S6. The red curves in the dispersions are the three acoustic modes. In both \( \gamma \)- and \( \beta \)-phases, the slopes of the acoustic phonons are steeper in Zr than in Hf oxynitride. This is indicative of a slower speed of sound in the Hf oxynitrides as compared to their Zr counterparts. Apart from this, there are two observable significant results from the phonon dispersion: (1) there is a phonon band gap in \( \gamma\)\text{-Hf}_2\text{ON}_2 and (2) \( \beta\)\text{-M}_2\text{O}_3\text{N}_4 have imaginary phonon frequencies near the \( \Gamma \) point.

In Figure 6a, the phonon band gap appears to be between optical phonons only; however, the phonon DOS on the right-hand side shows that the phonon branches up to the top of the lower phonons below the gap (i.e., up to \( \sim 250 \) cm\(^{-1}\)) are due to the vibration of Hf atoms only. Because there were 8 formula units of \( \gamma\)\text{-Hf}_2\text{ON}_2 in the simulation, the lattice constant of the simulated unit cell is larger than that of the primitive unit cell, which imposed back-folding of the acoustic phonons and hence these are observed as “optical-like” phonons in the dispersion. Indeed, these optical-like acoustic phonons are presented in all four materials, which can be confirmed by the spreading of the metal partial phonon DOS (magenta curves) in all diagrams.

The negative phonon modes (also known as soft modes) obtained from a DFPT method are related to lattice instability either due to ferroelectric behavior or due to pressure- or temperature-dependent phase transitions. \(^{27}\) No such study regarding the lattice instability of the \( \beta\)\text{-M}_2\text{O}_3\text{N}_4 has ever been

### Table 2. Static Dielectric Constant, Refractive Index, and Optical Anisotropy of the \( \gamma \)-Phase Oxynitrides

| \( \gamma\)\text{-Zr}_2\text{ON}_2 | \( \gamma\)\text{-Hf}_2\text{ON}_2 |
|-------------------------------|-------------------------------|
| **static optical constants**  |                               |
| \( \epsilon_x^{(0)}(0) \)     | 8.90                          | 7.59                          |
| \( \epsilon_y(0) \)           | 8.55                          | 7.29                          |
| \( \epsilon_z(0) \)           | 9.10                          | 7.74                          |
| \( n_a^{(0)}(0) \)            | 9.05                          | 7.71                          |
| \( n_b^{(0)}(0) \)            | 2.98                          | 2.75                          |
| \( n_c(0) \)                  | 2.92                          | 2.70                          |
| \( n_a(0) \)                  | 3.02                          | 2.78                          |
| \( n_b(0) \)                  | 3.00                          | 2.78                          |
| \( n_c(0) \)                  |                               |                               |
| **optical anisotropy**        |                               |                               |
| \( x \)                       | [0.961, 0.980]                | [0.961, 0.981]                |
| \( y \)                       | [1.022, 1.011]                | [1.021, 1.011]                |
| \( z \)                       | [1.017, 1.008]                | [1.017, 1.008]                |
reported before. However, it can be speculated that the small soft mode near the zone center of the $\beta$-phases is likely to be due to a ferroelectric characteristic. Ferroelectricity, which is characterized by a robust switchable polarization, occurs when there is a constant interplay of the constituent species such as rotations and distortions from their ideal sites in the lattice. The ferroelectric phase of a material is characterized by a long-range Coulomb attraction, which occurs in a low-symmetry phase at lower temperature, while at higher temperature short-range repulsion becomes dominant and a high-symmetry phase is stabilized.\textsuperscript{39,40} For example, in BaTiO$_3$, a typical ferroelectric oxide perovskite, three ferroelectric phase transitions occur: from cubic to tetragonal at 393 K, tetragonal to orthorhombic at 278 K, and from orthorhombic to rhombohedral at 183 K.\textsuperscript{39}

At this point, two important points should be noted: (1) $\beta$-phases, which are rhombohedral, are basically formed by substituting some of the O vacancies by N anions in the cubic MO$_2$ structure and the structure (X-ray diffraction data) looks similar to each other (hence the term "pseudo-cubic")\textsuperscript{2,22} and (2) as mentioned earlier, the building block of this structure (the Bevan cluster) has two types of metal cations, which create a constant struggle between the pseudo-cubic and rhombohedral metal sublattice to bring the symmetry to a perfect cubic or to further distort upon the application of some external force.\textsuperscript{21,41} Therefore, the $\beta$-phase is likely to rearrange to a highly symmetric cubic phase at a certain temperature, and because of the two dissimilar cations in the sublattice, there is likely to be relative movements that lead to the formation of electrical polarization as in oxide perovskites.\textsuperscript{42} While these are as yet only speculations, this certainly invites detailed experimental characterization in the near future.

The presence of a phonon band gap in $\gamma$-Hf$_2$ON$_2$ and the qualitative indication of a smaller speed of sound also invites further studies in this material. These are preliminary indications of the material having a small thermal conductivity value, which is desirable in the HCSC and in thermoelectric materials. However, the small phonon band gap in $\gamma$-Hf$_2$ON$_2$ makes it unsuitable as a hot carrier absorber material because one of the most critical conditions for a hot carrier absorber is to have a suppressed Klemens decay mechanism,\textsuperscript{43} an anharmonic scattering mechanism in which an optical phonon decays into two acoustic phonons of the same energy and equal and opposite momenta. Therefore, the minimum optical phonon frequency must be higher than twice the maximum acoustic phonon frequency to prevent the energy loss via Klemens decay—none of the studied oxynitrides meet this condition. Additionally, the higher $E_g$ values in these oxynitrides make them unsuitable as a bulk hot carrier absorber material. Nevertheless, a recent publication shows that a high $E_g$ material is a potential candidate for an energy-selective contact (ESC) of the HCSC concept.\textsuperscript{44} Therefore, there are many areas where the electronic and phononic properties of these oxynitrides can be exploited, for example, the ESCs.

5. CONCLUSIONS

Hafnium and zirconium oxynitrides have potential applications in many areas such as semiconducting, optoelectronic, and PV
devices. Here, we performed DFT calculations on electronic, optical, and phononic properties of the $\gamma$- and $\beta$-phases of Hf and Zr oxynitrides and present the consolidated results. The calculated lattice parameters, energy gap, and optical constant values match well with some available experimental and theoretical values. Our results show that the $\gamma$-phases have a purely indirect-type band gap and are characterized by a metallic d-state CB tail, while the $\beta$-phases have a pseudo-direct energy gap. We present various optical properties of the $\gamma$-phases and show that they are highly isotropic. The phononic properties of $\gamma$-Hf$_2$ON$_2$ exhibit a small gap in the phonon dispersion, and we observe soft phonon modes in $\beta$-M$_7$O$_8$N$_4$, indicating lattice instability. The emphasis is given if the phononic properties of these oxynitrides are favorable for the use as a HCSC absorber material. Our results show that they cannot be used as a bulk HCSC absorber material; however, they look suitable for the ESCs of the HCSC and in many other applications.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05649.

Cohesive energy and formation enthalpy for all phases; Brillouin zone shapes of the simulated structures; cutoff energy convergence test; partial electronic density of states in the whole spectra; Kohn–Sham orbitals for the Zr compounds; optical properties in the UV–vis–NIR

Figure 6. Phononic band dispersion. (a–d) $\gamma$-Hf$_2$ON$_2$, $\gamma$-Zr$_2$ON$_2$, $\beta$-Hf$_2$O$_3$N$_4$ and $\beta$-Zr$_2$O$_3$N$_4$, respectively. The right-hand side on each plot is the corresponding density of states.
region; and full phonon dispersion for all simulated compounds (PDF).

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B.T.: conceptualization, data curation, formal analysis, methodology, software, visualization, and writing (original draft); R.J.P.: resources, software, validation, and writing (review and editing); G.C.: resources, supervision, validation, and writing (review and editing); and S.S.: resources, supervision, validation, and writing (review and editing).

**Notes**

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