First-principles Calculations of Raman and Infrared Spectroscopy For Phase Identification and Strain Calibration of Hafnia.

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Using density functional perturbation theory (DFPT) we computed the phonon frequencies, Raman and IR activities of hafnia polymorphs (P4\textsuperscript{2}2\textsubscript{1}2\textsubscript{1}, Pca\textsubscript{2}1, Pmn\textsubscript{2}1, Pbca OI, brookite, and baddeleyite) for phase identification. We investigated the evolution of Raman and IR activities with respect to epitaxial strain and provide plots of frequency differences as a function of strain for experimental calibration and identification of the strain state of the sample. We found Raman signatures of different hafnia polymorphs: $\omega(A_1) = 300$ cm\textsuperscript{-1} for P4\textsuperscript{2}2\textsubscript{1}2\textsubscript{1}, $\omega(A_1) = 343$ cm\textsuperscript{-1} for Pca\textsubscript{2}1, $\omega(B_2) = 693$ cm\textsuperscript{-1} for Pmn\textsubscript{2}1, $\omega(A_g) = 513$ cm\textsuperscript{-1} for Pbca (OI), $\omega(A_g) = 384$ cm\textsuperscript{-1} for brookite, and $\omega(A_g) = 496$ cm\textsuperscript{-1} for baddeleyite. We also identified the Raman $B_{1g}$ mode, an anti-phase vibration of dipole moments, ($\omega(B_{1g}) = 784$ cm\textsuperscript{-1} for OI, $\omega(B_{1g}) = 784$ cm\textsuperscript{-1} for brookite) as the Raman signature of antipolar Pbca structures. We calculated a large splitting between longitudinal optical (LO) and transverse optical (TO) modes ($\Delta\omega_{\text{LO-TO}}(A_1) = 255$ cm\textsuperscript{-1} in Pca\textsubscript{2}1, and $\Delta\omega_{\text{LO-TO}}(A_1) = 263$ cm\textsuperscript{-1} in Pmn\textsubscript{2}1) to the same order as those observed in perovskite ferroelectrics, and related them to the anomalously large Born effective charges of Hf atoms ($Z^*(\text{Hf}) = 5.54$).

Hafnia is of great interest because of its compatibility with silicon and its robust ferroelectricity at the nanoscale. It has a high permittivity and has been proposed as a dielectric material for dynamic random access memories (DRAM) and logic devices\textsuperscript{1,2}. At ambient pressure and temperature it stabilizes in the monoclinic crystal structure (P2\textsubscript{1}/c)\textsuperscript{3}, but can also have different structures depending on temperature and pressure. At ambient pressure there are two high-temperature polymorphs: the tetragonal (P4\textsuperscript{2}2\textsubscript{1}2\textsubscript{1}), when 1700°C < T < 2600°C, and the cubic (Fm3m) when T > 2600°C\textsuperscript{4}. Other phases have been stabilized under different pressure, such as Pbca, when 5.9 GPa < P < 15 GPa, and Pnma when under P > 15 GPa\textsuperscript{4,5}, epitaxial strain\textsuperscript{6}, or doping\textsuperscript{7,8}.

Recent investigations have highlighted the possibility and importance of ferroelectricity in hafnia\textsuperscript{9–14}, and studies of yttrium-doped hafnia revealed the Pca\textsubscript{2}1 polymorph as the polar phase responsible for ferroelectricity\textsuperscript{15}. Antiferroelectricity has also been observed in doped hafnia\textsuperscript{16} and further theoretical studies have shown that the orthorhombic Pbca structure, which contains two Pca\textsubscript{2}1 cells with opposite oxygen displacement relative to the hafnia atoms, is the antiferroelectric orthorhombic structure\textsuperscript{11}. Hafnia is also of fundamental interest due to its fluorite-based structure, different from the wide class of well-studied perovskite ferroelectrics. One hindrance to the rapid development of hafnia ferroelectrics has been a lack of basic understanding of ferroelectricity.

Structural studies are usually based on X-ray diffraction (XRD) methods. Complementary to XRD, inelastic light scattering such as Raman or IR spectroscopy is also a tool that can be used to determine the structure and structural response of different hafnia phases. The latter approach reveals information about interatomic interaction, hence atomic arrangements, through the vibrational spectra. Epitaxial strain is important in thin films and it can affect the Raman frequencies and intensities. One of the advantages of Raman spectroscopy is that it can provide information about the strain on the sample once calibrated. Only Raman shifts and peak intensities are accessible experimentally thus the need of first-principles studies of atomic vibrations for symmetry assignment of Raman peaks. Although Raman and IR data are available from previous calculations of hafnia polymorphs\textsuperscript{17–19} they do not cover all the relevant phases, namely both polar orthorhombic phases or both antipolar orthorhombic phases. Furthermore, experimentally it is normal to observe mixture of different phases in hafnia such as baddeleyite and Pca\textsubscript{2}1\textsuperscript{20}, which makes the symmetry determination using Raman or IR spectroscopy crucial.

Our aim in this paper is to provide tools for experiments to identify the structure of hafnia and determine the epitaxial strain to which the sample is subject. Using DFPT we computed the phonon frequencies and their activities (Raman and IR) at different strain values ($\eta = [−3.0\%, −1.5\%, 0.0\%, 1.5\%, 3.0\%]$) for different hafnia polymorphs, namely baddeleyite, P4\textsuperscript{2}2\textsubscript{1}2\textsubscript{1}, Pca\textsubscript{2}1, Pbca (OI), and brookite. We tracked the evolution of phonon mode frequencies under strain, and provided means to identify the strain through identification of strain-induced frequency shifts of signature phonons.

We performed first-principles calculations using QUANTUM ESPRESSO\textsuperscript{21–24}, with optimized norm-conserving Vanderbilt (ONCV) pseudopotentials\textsuperscript{24}. The cell parameters and atomic positions were optimized using the local density approximation (LDA) with the Perdew-Zunger (PZ) exchange-correlation functional\textsuperscript{25},

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generated using the ONCVSP code. The plane-wave expansion is truncated using a cutoff energy of $E_{\text{cutoff}} = 1306.6$ eV, and the Brillouin zone was sampled using an $8 \times 8 \times 8$ Monkhorst-Pack grid. We calculated the Brillouin zone center phonon frequencies using density functional perturbation theory (DFPT) implemented in the QE/PH package. We considered the powder Raman spectra, with the Raman activity computed using Placzek approximation. We plotted the spectra by convoluting with a Gaussian shape function whose width is $5 \text{ cm}^{-1}$ estimated from experiments. Similar widths have been used in previous studies.

We set a coordinate system similar to the ones defined in Ref.6. We consider the epitaxy of the tetragonal case with a square substrate such as Yttria-stabilized zirconia (YSZ), with $z$ normal to the epitaxial plane, and $a$ and $b$ in registry with the epitaxial surface. Strain $\eta$ was applied by setting:

$$a_\eta = (1 + \eta)a_0,$$

where $a_0$ is the strain-free ground state lattice constant of the tetragonal phase. The out-of-plane lattice constant $(c)$ and the atomic positions were relaxed at each strain.

To validate the accuracy of our DFPT calculations, we compare the calculated Raman spectra of the strain-free baddeleyite and brookite to the measured Raman spectra (Fig. 1). The Raman spectrum of brookite was measured from a sample under hydrostatic pressure ($P = 5.9$ GPa). So, for fair comparison, the cell parameters and the atomic positions for our calculations for brookite were relaxed under the same pressure. The calculated spectra of baddeleyite and brookite match the experimentally measured spectra well (Fig. 1). For baddeleyite, the high intensity $A_g$ peaks (with $A_g = 495 \text{ cm}^{-1}$), the shoulder peak $B_g$ (with $B_g = 510 \text{ cm}^{-1}$), and the double peaks $B_g$ (with $B_g = 637 \text{ cm}^{-1}$) all closely match with experimental peaks; for brookite we can point to the high intensity $A_g$ peak (with $A_g = 384 \text{ cm}^{-1}$), the $B_{1g}$ peak (with $B_{1g} = 513 \text{ cm}^{-1}$), the double peaks $B_{3g}$ (with $B_{3g} = 593 \text{ cm}^{-1}$) and $B_{1g}$ (with $B_{1g} = 604 \text{ cm}^{-1}$). Our calculated spectra for baddeleyite, tetragonal and brookite also compare well with other calculations (see Supplementary Material, Fig. S1).

We plot the Raman spectra of the different strain-free hafnia polymorphs (Fig. 1, Fig. 2) to help with the identification of the crystal structures. The high intensity peaks of the Raman spectra can help in the identification of the structure symmetry. For example, the high intensity mode at $A_g = 496 \text{ cm}^{-1}$ is found only in baddeleyite. The Pmn2$_1$ structure can be identified using the high frequency $B_2$ (with $B_2 = 693 \text{ cm}^{-1}$) and $A_1$ (with $A_1 = 722 \text{ cm}^{-1}$) peaks. The Pca2$_1$ structure can be identified using the $A_g$ peak (with $A_g = 340 \text{ cm}^{-1}$) and the strong $A_1$ peak (with $A_1 = 670 \text{ cm}^{-1}$). The presence of these peaks can be used to identify the Pca2$_1$ structure. This is an advantage of the Raman (or IR) spectroscopy over the XRD given that phase identification using XRD can be harder due to the monoclinic and Pca2$_1$ phase mixtures and the overlap of XRD peaks, whereas with Raman spectroscopy the difference can be resolved easily. In Pbcn (O1) the signature modes are the strong $A_g$ peaks at $A_g = 513 \text{ cm}^{-1}$, and the double $A_g$ and $B_{2g}$ peaks at $A_g = 658 \text{ cm}^{-1}$ and $A_g = 668 \text{ cm}^{-1}$, respectively. Finally, in brookite the $A_g$ mode (with $A_g = 384 \text{ cm}^{-1}$) can be used as its fingerprint.

Additionally, we find a signature mode for antipolar polymorphs. This is the high frequency $B_{1g}$ peak (with $B_{1g} = 811 \text{ cm}^{-1}$ for brookite, or $B_{1g} = 791 \text{ cm}^{-1}$ for Pbcn O1). This mode is absent in the FE (Pca2$_1$ and Pmn2$_1$) structures and it is an anti-phase vibration of the $O$ atoms in neighboring cells of the Pbcn (Fig. 3). This anti-phase vibration of the $O$ atoms can be thought as an anti-phase collective motion of the dipole moments.

The splitting between longitudinal optical (LO) and transverse optical (TO) phonon modes is a subject of interest in ferroelectrics. Indeed, perovskite ferroelectrics are known to have phonon modes that exhibit giant LO-TO splittings. Using the rigorous definition of LO-TO splitting, we show that these large LO-TO splittings also occur in hafnia. In polar Pmn2$_1$ phase, the calcu-
The evolution of the phonon modes is not straightforward, and choices had to be made on the modes and exceptions such as: Z close to the nominal charge of O atoms (-2), with few exceptions such as: $Z^*_{\text{O}}(O1) = Z^*_{\text{Zr}}(O2) = -3.42$ in P4_2/mmc, $Z^*_{\text{Os}}(O1) = -3.15$ and $Z^*_{\text{Zr}}(O2) = -3.08$ in Pmn2_1, the Hf atoms have anomalously large dynamical charges up to 5.54. Other calculations also reported similar values. The three modes with large LO-TO splitting mentioned earlier all have in common the antiphase motion between the Hf and O.

The constraint on the lattice constant imposed by the substrate affects the interatomic distances in the sample, which not only shifts the phonon frequencies but also changes the Raman and IR intensities. The shift in Raman or IR frequencies thus indicates the strains in a hafnia film. The evolution of phonon modes with respect to strain can be tracked using correspondence between the phonon eigenvectors at each strain following the approach in Ref.33. Firstly, the phonon eigenvectors at strain $\eta_2$ were projected to the eigenvectors at strain $\eta_1$:

$$\epsilon^{i\alpha}_n(\eta_2) = \sum_m a_{mn}\epsilon^{i\alpha}_m(\eta_1),$$

where $m$ and $n$ are the phonon mode indices, $i$ and $\alpha$ are the atoms and the direction indices respectively; the coefficient $a_{mn} = \sum_i (\epsilon^{i\alpha}_m(\eta_1)\epsilon^{i\alpha}_n(\eta_2))$ indicates the correlation or projection of phonon eigenmode $n$ at strain $\eta_2$ to the eigenmodes at strain $\eta_1$. Then by choosing the mode with the highest correspondence coefficient $a_{mn}$ (Eq. 2), i.e. the mode with the highest correspondence probability to mode $n$ denoted by $\omega_m(\eta)$, we assign $\omega_n(\eta_2) \rightarrow \omega_m(\eta_1)$.

The calculation of the frequency difference is straightforward once equipped with the strain-to-strain mode correspondence (Eq.2):

$$\Delta\omega_{l,n}(\eta) = \omega_l(\eta) - \omega_n(\eta),$$

where it should be understood that $\omega_l(\eta)$ and $\omega_n(\eta)$ are the phonon modes that correspond to $\omega_l(0)$ and $\omega_n(0)$ at zero strain, respectively. $\Delta\omega_{l,n}(\eta)$ changing sign means that the order of the modes considered switched.

FIG. 2. Raman spectra of (a) P4_2/mmc, (b) Pmn2_1, (c) Pca2_1, and (d) Pbca (OI). We convoluted the spectra using a Gaussian shape function of width 5 cm$^{-1}$ estimated from experiments. The squares indicate modes chosen to compute the frequency differences (Fig.4).

FIG. 3. The atomic displacements corresponding to the high frequency $B_{1g}$ mode in Pbca AFE structures. The larger spheres represent the Hf atoms and the smaller spheres the O atoms. The blue arrows on the atoms indicate the direction of the atomic vibrations. The arrows on the bottom right corner show the crystallographic directions.

FIG. 4. Evolution of frequency difference with respect to epitaxial strain for selected modes of (a) baddeleyite, (b) P4_2/mmc, (c) Pmn2_1, (d) Pca2_1, (e) Pbca OI, and f brookite. The star, diamond, and triangle symbols in (a), (b), and (f) are frequency differences using data from Ref.31, Ref.17, and Ref.35, respectively. The blue and red curves are calibration using IR and Raman active modes, respectively. The Raman modes used for calibrations are marked by the empty squares on the Raman spectra in Fig1 and the IR modes are marked as blue modes in Table S3–S8 (see Supplementary Material).

The evolution of the phonon modes is not straightforward, and choices had to be made on the modes...
used to compute the frequency difference (Fig.4). The modes chosen (Fig. 1, and Fig.2) were modes with non-negligible Raman or IR intensities and the ones showing monotonic behavior if possible, within a range of 200 cm$^{-1}$ for plotting purposes. In Fig.4 we used results from studies with samples that are either under hydrostatic pressure$^{31}$ or doped hafnia$^{35}$ for comparison. For the case where doping helps with the stabilization of a particular polymorph, peaks associated to defects or dopants were identified$^{35}$ so the comparison with the remaining peaks, probably from the tetragonal polymorph, with our calculation results can be made.

For the comparison of Pbca brookite spectra, the Raman spectra in Ref.31 were obtained under hydrostatic pressure. We performed two different first-principles calculations for the brookite phase, one at ambient pressure and one under 5.9 GPa. We find that pressure hardens the individual Raman modes, as expected. But the difference between two modes ($\Delta \omega_{l,n}$) for the system at ambient pressure was similar to $\Delta \omega_{l,n}$ for the system under hydrostatic pressure. It is thus fair to compare $\Delta \omega_{l,n}$ from the experiment under pressure with $\Delta \omega_{l,n}$ from DFPT at ambient pressure (Fig.4f).

For most cases, the frequency difference between two peaks changes linearly with strain, such as $\Delta \omega_{B_{1g},B_{2g}}(\eta) = 80 + 4.2 \eta$ for the Raman active modes chosen in brookite or $\Delta \omega_{A_{2g},B_{1g}}(\eta) = 89 + 5.9 \eta$ for the Raman active modes chosen in Pmn2$_1$. On the other hand, for the Pca2$_1$ and baddeleyite the frequency difference is better described by a quadratic polynomial of the strain $\eta$:

$$\Delta \omega_{A_{2g},B_{1g}}(\eta) = 142 - 13.7 \eta + 2 \eta^2, \quad (4)$$

for the Raman active modes chosen in baddeleyite, and

$$\Delta \omega_{A_{1g},B_{1g}}(\eta) = 15 + 14.1 \eta + 3.7 \eta^2 \quad (5)$$

for Pca2$_1$.

Now we briefly discuss an interesting comparison between hafnia and zirconia, two isomorphous compounds$^3$. Recent studies on ZrO$_2$ combined experimental measurements and computations of Raman spectra to identify the zirconia polymorphs using Raman$^{36}$. The Raman spectra of monoclinic hafnia and zirconia are similar, e.g. the $A_g$ peak at $\omega(A_g) = 495$ cm$^{-1}$ in hafnia and the $A_g$ peak at $\omega(A_g) = 470$ cm$^{-1}$ in zirconia, or the $B_g$ peak at $\omega(B_g) = 637$ cm$^{-1}$ in hafnia compared to $\omega(B_g) = 598$ cm$^{-1}$ in zirconia. The quantitative mismatch between the spectra in hafnia and zirconia (25 cm$^{-1}$ for $A_g$ and 30 cm$^{-1}$ for $B_g$) can be attributed to differences in the interatomic force constant (IFC) resulting from the difference in the cation. Interestingly, despite these quantitative discrepancies in the Raman frequencies of hafnia and zirconia, the frequency differences $\Delta \omega_{l,n}$ are comparable. In monoclinic hafnia for example, the frequency difference $\Delta \omega_{A_{1g},B_{1g}} = 142$ cm$^{-1}$ compares well with $\Delta \omega_{A_{1g},B_{1g}} = 140$ cm$^{-1}$ in zirconia, and in tetragonal the frequency difference $\Delta \omega_{E_{g},B_{1g}} = 130$ cm$^{-1}$ in hafnia is a close match to $\Delta \omega_{E_{g},B_{1g}} = 135$ cm$^{-1}$ in zirconia.

We computed the phonon frequencies of P4$_{2}nm$, Pmn2$_1$, Pca2$_1$, Pbca (OI), brookite, and baddeleyite using DFPT at different values of epitaxial strains. We found that Raman spectra can be used to identify the symmetry or phases of hafnia, namely $\omega(A_{1g}) = 300$ cm$^{-1}$ for P4$_{2}nm$, $\omega(A_{1g}) = 343$ cm$^{-1}$ for Pca2$_1$, $\omega(B_{2g}) = 693$ cm$^{-1}$ for Pmn2$_1$, $\omega(A_{g}) = 513$ cm$^{-1}$ for Pbca (OI), $\omega(A_{g}) = 384$ cm$^{-1}$ for brookite, and $\omega(A_{g}) = 496$ cm$^{-1}$ for baddeleyite. We also identified the Raman signature of AFE structures as the $\omega(B_{1g}) = 784$ cm$^{-1}$ peak for brookite or the $\omega(B_{1g}) = 758$ cm$^{-1}$ peak for Pbca (OI). The presence (or absence) of this Raman signal can be used to distinguish between AFE and FE orthorhombic hafnia. Further, we showed the evolution of frequency differences between selected normal mode frequencies with respect to strain for calibration purposes and identification of strain state of the hafnia crystal.

**SUPPLEMENTARY MATERIAL**

Comparison of bookite Raman spectra at ambient pressure(Fig.S1), the calculated Born effective charges (Table S1–S2), the infrared frequencies and IR activities of different hafnia polymorphs (Table S3–S8).

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$^1$A. I. Kingon, J.-P. Maria, and S. K. Streiffer, “Alternative dielectrics to silicon dioxide for memory and logic devices,” Nature **406**, 1032–1038 (2000).

$^2$G. D. Wilk, R. M. Wallace, and J. M. Anthony, “High- gate dielectrics: Current status and materials properties considerations,” Journal of Applied Physics **89**, 5243–5275 (2001).

$^3$R. Ruh and P. W. R. Corfield, “Crystal Structure of Monoclinic Hafnia and Comparison with Monoclinic Zirconia,” Journal of the American Ceramic Society **53**, 126–129 (1970).

$^4$O. Ohtaka, H. Fuku, T. Kunisada, T. Fujisawa, K. Fuakoshi, W. Utsumi, T. Irifune, K. Kuroda, and T. Kikegawa, “Phase relations and volume changes of hafnia under high pressure and high temperature,” Journal of the American Ceramic Society **84**, 1369–1373 (2001).
A. Comparison of Raman spectra

FIG. S1. Calculated Raman spectrum of brookite (blue) compared to theoretical Raman spectrum (red) at ambient pressure. The calculated spectrum was convoluted with a Gaussian shape function of width 5 cm$^{-1}$ estimated from experiments.
### B. Born effective charges

| Phase   | Atoms | Z\(^x\) | Z\(^y\) | Z\(^z\) | Z\(^xy\) | Z\(^yx\) | Z\(^xz\) | Z\(^zx\) | Z\(^yz\) | Z\(^zy\) | Z\(^zz\) | Nominal charge |
|---------|-------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|----------------|
| Baddeleyite |
| Hf1     | 5.33  | -0.39  | 0.23   | -0.12  | 5.34   | 0.15   | 0.24   | 0.35   | 4.75   | 4       |
| Hf2     | 5.33  | 0.39   | 0.23   | 0.12   | 5.34   | -0.15  | 0.24   | -0.35  | 4.75   | 4       |
| O1      | -2.95 | -1.05  | -0.22  | -1.30  | -2.60  | 0.64   | -0.19  | 0.63   | -2.22  | -2      |
| O2      | -2.95 | 1.05   | -0.22  | 1.30   | -2.60  | -0.64  | -0.19  | -0.63  | -2.22  | -2      |
| O3      | -2.37 | -0.11  | -0.01  | -0.18  | -2.74  | -0.35  | -0.05  | -0.42  | -2.53  | -2      |
| O4      | -2.37 | 0.11   | -0.01  | 0.18   | -2.74  | 0.35   | -0.05  | 0.42   | -2.53  | -2      |
| P4\(^2\)nmc |
| Hf      | 5.54  | 0      | 0      | 0      | 5.54   | 0      | 0      | 0      | 4.84   | 4       |
| O1      | -2.12 | 0      | 0      | 0      | -3.42  | 0      | 0      | 0      | -2.42  | -2      |
| O2      | -3.42 | 0      | 0      | 0      | -2.12  | 0      | 0      | 0      | -2.42  | -2      |
| Pmn\(^2\)1 |
| Hf1     | 5.35  | 0      | 0      | 0      | 5.02   | 0.10   | 0      | 0.33   | 5.11   | 4       |
| Hf2     | 5.35  | 0      | 0      | 0      | 5.02   | -0.10  | 0      | -0.33  | 5.11   | 4       |
| O1      | -3.15 | 0      | 0      | 0      | -2.67  | -0.80  | 0      | -0.86  | -2.03  | -2      |
| O2      | -3.15 | 0      | 0      | 0      | -2.67  | 0.80   | 0      | 0.86   | -2.03  | -2      |
| O3      | -2.20 | 0      | 0      | 0      | -2.35  | 0.04   | 0      | -0.05  | -3.08  | -2      |
| O4      | -2.20 | 0      | 0      | 0      | -2.35  | -0.04  | 0      | 0.05   | -3.08  | -2      |

**TABLE S1.** Computed Born effective charges for baddeleyite, P4\(^2\)nmc and Pmn\(^2\)1 hafnia polymorphs compared to their nominal charges. Hf1, Hf2 (resp. O1, O2, O3, and O4) are the symmetrically inequivalent Hf (resp. O) atoms in the HfO\(_2\) unit cell.

### C. IR frequencies

Here we list the computed IR frequencies, their intensities and their symmetry.
| Phase     | Atoms | $Z_{xx}^*$ | $Z_{xy}^*$ | $Z_{xz}^*$ | $Z_{yx}^*$ | $Z_{yy}^*$ | $Z_{yz}^*$ | $Z_{zx}^*$ | $Z_{zy}^*$ | Nominal charge |
|-----------|-------|------------|------------|------------|------------|------------|------------|------------|------------|----------------|
| **Pca2$_1$** | Hf1   | 5.17       | 0.00       | -0.035     | -0.35      | 5.49       | -0.14      | 0.05       | -0.22      | 4.97           | 4              |
|           | Hf2   | 5.17       | 0.00       | 0.035      | -0.35      | 5.49       | 0.14       | -0.05      | 0.22       | 4.97           | 4              |
|           | Hf3   | 5.17       | 0.00       | -0.035     | 0.35       | 5.49       | 0.14       | 0.05       | 0.22       | 4.97           | 4              |
|           | Hf4   | 5.17       | 0.00       | 0.035      | 0.35       | 5.49       | -0.14      | -0.05      | -0.22      | 4.97           | 4              |
|           | O1    | -2.49      | -0.96      | 0.31       | -0.76      | -2.96      | -0.69      | 0.31       | -0.63      | -2.46          | -2             |
|           | O2    | -2.49      | -0.96      | -0.31      | -0.76      | -2.96      | 0.69       | -0.31      | 0.63       | -2.46          | -2             |
|           | O3    | -2.49      | 0.96       | 0.31       | 0.76       | -2.96      | 0.69       | 0.31       | 0.63       | -2.46          | -2             |
|           | O4    | -2.49      | 0.96       | -0.31      | 0.76       | -2.96      | -0.69      | -0.31      | -0.63      | -2.46          | -2             |
|           | O5    | -2.68      | 0.13       | 0.25       | 0.07       | -2.52      | -0.19      | 0.29       | -0.13      | -2.50          | -2             |
|           | O6    | -2.68      | 0.13       | -0.25      | 0.07       | -2.52      | 0.19       | -0.29      | 0.13       | -2.50          | -2             |
|           | O7    | -2.68      | -0.13      | 0.25       | -0.07      | -2.52      | 0.19       | 0.29       | 0.13       | -2.50          | -2             |
|           | O8    | -2.68      | -0.13      | -0.25      | -0.07      | -2.52      | -0.19      | -0.29      | -0.13      | -2.50          | -2             |
| **Pbca (O1)** | Hf1   | 5.28       | 0.34       | 0.13       | 0.34       | 4.78       | -0.03      | 0.30       | -0.08      | 5.43           | 4              |
|           | Hf2   | 5.28       | 0.34       | -0.13      | 0.34       | 4.78       | 0.03       | -0.30      | 0.08       | 5.43           | 4              |
|           | Hf3   | 5.28       | -0.34      | 0.13       | -0.34      | 4.78       | 0.03       | 0.30       | 0.08       | 5.43           | 4              |
|           | Hf4   | 5.28       | -0.34      | -0.13      | -0.34      | 4.78       | -0.03      | -0.30      | -0.08       | 5.43           | 4              |
|           | O1    | -2.56      | -0.87      | -1.14      | -0.87      | -2.23      | 0.01       | -0.89      | 0.10       | -3.02          | -2             |
|           | O2    | -2.56      | -0.87      | 1.14       | -0.87      | -2.23      | -0.01      | 0.89       | -0.10      | -3.02          | -2             |
|           | O3    | -2.56      | 0.87       | -1.14      | 0.87       | -2.23      | -0.01      | -0.89      | 0.10       | -3.02          | -2             |
|           | O4    | -2.56      | 0.87       | 1.14       | 0.87       | -2.23      | 0.01       | 0.89       | 0.10       | -3.02          | -2             |
|           | O5    | -2.73      | 0.28       | -0.12      | 0.41       | -2.55      | -0.10      | -0.07      | 0.02       | -2.41          | -2             |
|           | O6    | -2.73      | 0.28       | 0.12       | 0.41       | -2.55      | 0.10       | 0.07       | 0.02       | -2.41          | -2             |
|           | O7    | -2.73      | -0.28      | -0.12      | -0.41      | -2.55      | 0.10       | -0.07      | 0.02       | -2.41          | -2             |
|           | O8    | -2.73      | -0.28      | 0.12       | -0.41      | -2.55      | -0.10      | 0.07       | -0.02      | -2.41          | -2             |
| **Brookite** | Hf1   | 4.89       | 0.24       | -0.02      | 0.04       | 5.46       | 0.39       | -0.13      | -0.00      | 5.31           | 4              |
|           | Hf2   | 4.89       | 0.24       | 0.02       | 0.04       | 5.46       | -0.39      | 0.13       | 0.00       | 5.31           | 4              |
|           | Hf3   | 4.89       | -0.24      | -0.02      | -0.04      | 5.46       | -0.39      | -0.13      | 0.00       | 5.31           | 4              |
|           | Hf4   | 4.89       | -0.24      | 0.02       | -0.04      | 5.46       | 0.39       | 0.13       | -0.00      | 5.31           | 4              |
|           | O1    | -2.49      | -0.04      | 0.36       | -0.09      | -2.49      | 0.04       | 0.31       | 0.01       | -2.76          | -2             |
|           | O2    | -2.49      | -0.04      | -0.36      | -0.09      | -2.49      | -0.04      | -0.31      | -0.01      | -2.76          | -2             |
|           | O3    | -2.49      | 0.04       | 0.36       | 0.09       | -2.49      | -0.04      | 0.31       | -0.01      | -2.76          | -2             |
|           | O4    | -2.49      | 0.04       | -0.36      | 0.09       | -2.49      | 0.04       | -0.31      | 0.01       | -2.76          | -2             |
|           | O5    | -2.39      | -0.56      | 0.31       | -0.62      | -2.97      | -0.80      | 0.32       | -0.98      | -2.55          | -2             |
|           | O6    | -2.39      | -0.56      | -0.31      | -0.62      | -2.97      | 0.80       | -0.32      | 0.98       | -2.55          | -2             |
|           | O7    | -2.39      | 0.56       | 0.31       | 0.62       | -2.97      | 0.80       | 0.32       | 0.98       | -2.55          | -2             |
|           | O8    | -2.39      | 0.56       | -0.31      | 0.62       | -2.97      | -0.80      | -0.32      | -0.98      | -2.55          | -2             |

**TABLE S2.** Computed Born effective charges for Pca$_2$$_1$, Pbca (O1) and brookite hafnia polymorphs compared to their nominal charges. Hf1, Hf2, Hf3 and Hf4 (resp. O1, O2, O3, and O4) are the symmetrically inequivalent Hf (resp. O) atoms in the HfO$_2$ unit cell.
| Mode | Freq (cm$^{-1}$) | IR (arb. u.) |
|------|-----------------|--------------|
| $q \rightarrow [001]$ |                |              |
| $B_u$ | 236             | 22.84        |
| $A_u$ | 256             | 20.18        |
| $B_u$ | 320             | 41.87        |
| $A_u$ | 361             | 39.70        |
| $B_u$ | 370             | 7.43         |
| $A_u$ | 411             | 24.29        |
| $A_u$ | 499             | 12.55        |
| $B_u$ | 516             | 19.40        |
| $A_u$ | 614             | 12.53        |
| $B_u$ | 651             | 76.23        |
| $B_u$ | 743             | 16.88        |
| $q \rightarrow [010]$ |                |              |
| $A_u$ | 95              | 19.57        |
| $B_u$ | 95              | 19.57        |
| $A_u$ | 462             | 35.04        |
| $A_u$ | 462             | 35.04        |
| $A_2u$ | 627            | 39.86        |
| $E_u$ | 246             | 2.62         |
| $A_2u$ | 324            | 39.86        |
| $E_u$ | 462             | 35.04        |
| $E_u$ | 462             | 35.04        |
| $A_2u$ | 627            | 39.86        |

TABLE S3. Frequencies of IR-active modes in baddeleyite. Modes colored in blue are the modes used to compute frequency differences (see text).

| Mode | Freq (cm$^{-1}$) | IR (arb. u.) |
|------|-----------------|--------------|
| $q \rightarrow [001]$ |                |              |
| $B_u$ | 250             | 25.10        |
| $B_1$ | 300             | 32.60        |
| $B_2$ | 451             | 24.87        |
| $B_1$ | 492             | 10.10        |
| $A_1$ | 587             | 3.01         |
| $B_1$ | 701             | 2.10         |
| $A_1$ | 722             | 43.82        |
| $q \rightarrow [010]$ |                |              |
| $A_1$ | 177             | 6.80         |
| $B_2$ | 250             | 25.10        |
| $A_1$ | 254             | 3.80         |
| $A_1$ | 364             | 2.93         |
| $B_1$ | 432             | 3.06         |
| $A_1$ | 451             | 31.75        |
| $B_2$ | 451             | 24.87        |
| $A_1$ | 606             | 2.84         |
| $B_1$ | 632             | 20.16        |
| $B_1$ | 738             | 20.90        |

TABLE S4. Frequencies of IR-active modes for P4$_{2}^{\text{nmc}}$. Modes colored in blue are the modes used to compute frequency differences (see text).

| Mode | Freq (cm$^{-1}$) | IR (arb. u.) |
|------|-----------------|--------------|
| $q \rightarrow [001]$ |                |              |
| $B_2$ | 250             | 25.10        |
| $B_1$ | 300             | 32.60        |
| $B_2$ | 451             | 24.87        |
| $B_1$ | 492             | 10.10        |
| $A_1$ | 587             | 3.01         |
| $B_1$ | 701             | 2.10         |
| $A_1$ | 722             | 43.82        |
| $q \rightarrow [010]$ |                |              |
| $A_1$ | 177             | 6.80         |
| $A_1$ | 254             | 3.80         |
| $A_1$ | 364             | 2.93         |
| $B_1$ | 432             | 3.06         |
| $A_1$ | 451             | 31.75        |
| $B_2$ | 451             | 24.87        |
| $A_1$ | 606             | 2.84         |
| $B_1$ | 632             | 20.16        |
| $B_1$ | 738             | 20.90        |

TABLE S5. Frequencies of IR-active modes for Pmn2$_1$. Modes colored in blue are the modes used to compute frequency differences (see text).
TABLE S6. Frequencies of IR-active modes for Pca2₁. Modes colored in blue are the modes used to compute frequency differences (see text).

| Mode | Freq (cm⁻¹) | IR (arb. u.) | Mode | Freq (cm⁻¹) | IR (arb. u.) | Mode | Freq (cm⁻¹) | IR (arb. u.) |
|------|-------------|--------------|------|-------------|--------------|------|-------------|--------------|
| B₁   | 144         | 1.06         | A₁   | 122         | 2.18         | A₁   | 122         | 2.18         |
| B₁   | 237         | 40.77        | A₁   | 163         | 8.47         | B₁   | 144         | 1.06         |
| B₁   | 248         | 1.29         | A₁   | 260         | 2.19         | A₁   | 163         | 8.47         |
| B₂   | 275         | 37.59        | B₂   | 275         | 37.59        | B₁   | 237         | 40.77        |
| B₂   | 335         | 2.14         | B₁   | 305         | 2.09         | B₁   | 248         | 1.29         |
| B₂   | 393         | 50.69        | A₁   | 333         | 5.98         | A₁   | 260         | 2.19         |
| A₁   | 397         | 49.25        | B₂   | 335         | 2.14         | A₁   | 333         | 5.98         |
| A₁   | 431         | 3.16         | q →[010] | 342        | 46.83        | q →[100] | 342        | 46.83        |
| B₂   | 490         | 1.94         | B₂   | 393         | 50.69        | B₁   | 397         | 49.25        |
| B₁   | 532         | 8.19         | A₁   | 471         | 19.92        | A₁   | 471         | 19.92        |
| A₁   | 593         | 8.10         | A₁   | 471         | 19.92        | B₁   | 532         | 8.19         |
| B₁   | 644         | 3.79         | B₁   | 510         | 4.39         | A₁   | 606         | 1.95         |
| A₁   | 676         | 75.48        | A₁   | 606         | 1.95         | B₂   | 610         | 22.60        |
| B₁   | 747         | 7.78         | B₂   | 644         | 3.79         | B₂   | 692         | 22.93        |
| A₁   | 802         | 15.35        | B₁   | 652         | 49.35        | B₂   | 722         | 50.20        |
| B₁   | 806         | 2.00         | B₁   | 796         | 53.18        | B₁   | 747         | 7.78         |

TABLE S7. Frequencies of IR-active modes in Pbca OI. Modes colored in blue are the modes used to compute frequency differences (see text).
| Mode | Freq (cm\(^{-1}\)) | IR (arb. u.) | Mode | Freq (cm\(^{-1}\)) | IR (arb. u.) | Mode | Freq (cm\(^{-1}\)) | IR (arb. u.) |
|------|-------------------|-------------|------|-------------------|-------------|------|-------------------|-------------|
| B\(_{2u}\) | 191 | 17.37 | B\(_{2u}\) | 191 | 17.37 | B\(_{3u}\) | 253 | 8.16 |
| B\(_{2u}\) | 224 | 5.85 | B\(_{2u}\) | 224 | 5.85 | B\(_{3u}\) | 263 | 79.62 |
| B\(_{3u}\) | 253 | 8.16 | B\(_{1u}\) | 280 | 71.48 | B\(_{1u}\) | 280 | 71.48 |
| B\(_{3u}\) | 263 | 79.64 | B\(_{3u}\) | 319 | 2.92 | B\(_{3u}\) | 385 | 88.62 |
| B\(_{1u}\) | 323 | 2.28 | B\(_{2u}\) | 363 | 51.56 | B\(_{1u}\) | 392 | 82.96 |
| B\(_{2u}\) | 363 | 51.56 | B\(_{2u}\) | 368 | 55.47 | B\(_{2u}\) | 423 | 1.81 |
| B\(_{2u}\) | 368 | 55.47 | B\(_{1u}\) | 392 | 82.96 | B\(_{1u}\) | 425 | 33.01 |
| B\(_{3u}\) | 385 | 88.62 | B\(_{1u}\) | 425 | 33.01 | B\(_{1u}\) | 506 | 8.66 |
| B\(_{2u}\) | 441 | 30.44 | B\(_{2u}\) | 441 | 30.44 | B\(_{3u}\) | 555 | 21.39 |
| B\(_{1u}\) | 499 | 1.97 | B\(_{1u}\) | 506 | 8.66 | B\(_{2u}\) | 571 | 19.38 |
| B\(_{3u}\) | 555 | 21.39 | B\(_{3u}\) | 517 | 16.09 | B\(_{1u}\) | 646 | 7.35 |
| B\(_{2u}\) | 594 | 8.16 | B\(_{2u}\) | 594 | 8.16 | B\(_{2u}\) | 669 | 12.62 |
| B\(_{1u}\) | 620 | 31.91 | B\(_{1u}\) | 646 | 7.35 | B\(_{3u}\) | 683 | 133.57 |
| B\(_{1u}\) | 703 | 66.91 | B\(_{3u}\) | 658 | 85.45 | B\(_{1u}\) | 726 | 2.32 |
| B\(_{1u}\) | 750 | 102.39 | B\(_{1u}\) | 726 | 2.32 | B\(_{3u}\) | 752 | 17.74 |

TABLE S8. Frequencies of IR-active modes in brookite. Modes colored in blue are the modes used to compute frequency differences (see text).
REFERENCES

[S1] B. Zhou, H. Shi, X. D. Zhang, Q. Su, and Z. Y. Jiang, “The Simulated Vibrational Spectra of HfO$_2$ Polymorphs,” Journal of Physics D: Applied Physics 47, 115502 (2014).