Raman and Infrared Spectroscopy For Phase Identification and Strain Calibration of HfO$_2$.

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Using density functional perturbation theory (DFPT) we computed the phonon frequencies, Raman and IR activities of hafnia polymorphs (P4$_2$mm, Pca$_2$, Pmn$_2$, 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: $\omega(A_{1g}) = 300$ cm$^{-1}$ for P4$_2$mm , $\omega(A_1) = 343$ cm$^{-1}$ for Pca$_2$ , $\omega(B_2) = 693$ cm$^{-1}$ for Pmn$_2$ , $\omega(A_g) = 513$ 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 peak $B_{1g}$ mode, an anti-phase vibration of dipole moments, ($\omega(B_{1g}) = 758$ cm$^{-1}$ for OI, $\omega(B_{1g}) = 784$ cm$^{-1}$ for brookite) as the Raman signature of antiferroelectric 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$^{-1}$ in Pca$_2$, and $\Delta \omega_{\text{LO-TO}}(A_1) = 263$ cm$^{-1}$ in Pmn$_2$ ) to the same order as those observed in perovskite ferroelectrics, and related them to the anomalously large Born effective charges of Hf atoms ($Z^*$(Hf) = 5.54).

Hafnia is of great interest because of its compatibility with silicon and its robust ferroelectricity at the nanoscale. Recent investigations have highlighted the possibility and importance of ferroelectricity in hafnia$^{1-6}$. It 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, although there has been significant progress$^7$.

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$^{8-10}$ they do not cover all the relevant phases, namely both polar orthorhombic phases or both antipolar orthorhombic phases.

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$_2$mm , Pmn$_2$, Pca$_2$, 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$^{11-13}$, with optimized norm-conserving Vanderbilt (ONCV) pseudopotentials$^{14}$. The cell parameters and atomic positions were optimized using the local density approximation (LDA) with the Perdew-Zunger (PZ) exchange-correlation functional$^{15}$, generated using the oncvvpsp code$^{14}$. 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$^{16}$. We calculated the Brillouin zone center phonon frequencies using density functional perturbation theory (DFPT)$^{17}$ implemented in the QE/PH package$^{11-13}$.

We set a coordinate system similar to the ones defined in Ref.$^{18}$. 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 compared the calculated Raman spectra of the strain-free baddeleyite and brookite to the measured Raman spectra$^{19}$ (Fig.1). The Raman spectrum of brookite$^{19}$ was measured from a sample under hydrostatic pressure

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of $P = 5.9$ 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 ($\omega(A_g) = 495$ cm$^{-1}$), the shoulder peak $B_g$ ($\omega(B_g) = 510$ cm$^{-1}$), and the double peaks $B_g$ ($\omega(B_g) = 637$ cm$^{-1}$) and $A_g$ ($\omega(A_g) = 670$ cm$^{-1}$) all closely match with experimental peaks; for brookite we can point to the high intensity $A_g$ peak ($\omega(A_g) = 384$ cm$^{-1}$), the $B_{1g}$ peak ($\omega(B_{1g}) = 513$ cm$^{-1}$), the double peaks $B_{3g}$ ($\omega(B_{3g}) = 593$ cm$^{-1}$) and $B_{1g}$ ($\omega(B_{1g}) = 604$ cm$^{-1}$). Our calculated spectra for baddeleyite, tetragonal and brookite also compare well with other calculations.

Additionally, we find a signature mode for antipolar polymorphs. This is the high frequency $B_{1g}$ peak ($\omega(B_{1g}) = 811$ cm$^{-1}$ for brookite, or $\omega(B_{1g}) = 791$ cm$^{-1}$ for Pbca OI). 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 Pbca (Fig.3). This anti-phase vibration of the O atoms can be thought as an anti-phase collective motion of the dipole moments.

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 $\omega(A_g) = 496$ cm$^{-1}$ is found only in baddeleyite. The Pmn2$_1$ structure can be identified using the high frequency $B_2$ ($\omega(B_2) = 693$ cm$^{-1}$) and $A_1$ ($\omega(A_1) = 722$ cm$^{-1}$) peaks. The Pca2$_1$ structure can be identified using the $A_1$ peak ($\omega = 340$ cm$^{-1}$). Although there is a peak around that frequency in baddeleyite, XRD data can be used to differentiate between the monoclinic and the orthorhombic structure. In Pbca (OI) the signature mode is the strong $A_g$ peak at $\omega(A_g) = 513$ cm$^{-1}$. Finally, in brookite the $A_g$ mode ($\omega(A_g) = 384$ cm$^{-1}$) can be used as its fingerprint.
field induced by atomic displacements. Perovskite ferroelectrics are known to have phonon modes that exhibit giant LO-TO splittings\textsuperscript{20}. Using the rigorous definition of LO-TO splitting\textsuperscript{21}, we show that these large LO-TO splittings also occur in hafnia. In polar Pmn2\textsubscript{1} phase, the calculated LO-TO splitting is $\Delta \omega_{\text{LO-TO}}(A_1) = 263$ cm\textsuperscript{-1} for the high frequency $A_1$ mode ($\omega(A_1) = 722$ cm\textsuperscript{-1}); for the Pca2\textsubscript{1} phase we computed the LO-TO splitting to be $\Delta \omega_{\text{LO-TO}}(A_1) = 255$ cm\textsuperscript{-1} for $\omega(A_1^\text{Pca2}) = 676$ cm\textsuperscript{-1} and $\Delta \omega_{\text{LO-TO}}(B_2^\text{Pca2}) = 146$ cm\textsuperscript{-1} for the $B_2^\text{Pca2}$ mode at $\omega(B_2^\text{Pca2}) = 722$ cm\textsuperscript{-1} (Fig.2). These large LO-TO splittings can be attributed to the unusually large Born effective charge ($Z^*$) of Hf atoms in hafnia (see Supplementary Materials). Although the Born effective charges $Z^*(O)$ are close to the nominal charge of O atoms (-2), with few exceptions such as: $Z^*_{yy}(O1) = -3.42$ in P4\textsubscript{2}nm, $Z^*_{zz}(O1) = -3.15$ and $Z^*_{zz}(O2) = -3.08$ in Pmn2\textsubscript{1}, the Hf atoms have anomalously large dynamical charges that can be of the order of 5.54. Other calculations also reported similar values.\textsuperscript{10,22} 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 can thus indicate the strains in the 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.21. Firstly, the phonon eigenvectors at strain $\eta_2$ were projected to the eigenvectors at strain $\eta_1$:

$$
e_n^{\text{mn}}(\eta_2) = \sum_m a_m n^{\text{in}}_m(\eta_1),$$

where $m$ and $n$ are the phonon mode indices, $i$ and $\alpha$ are the atoms and the direction indices respectively; the coefficient $a_{mn} = \sum_i \langle e_n^{\text{in}}(\eta_1)|e_m^{\text{in}}(\eta_2) \rangle$ 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 maximum coefficient $a_{mn}$ (Eq. 2), i.e. the mode with the highest correspondence probability to mode $n$ denoted by $\omega_n^{\text{in}}$, we assign $\omega_n^{\text{in}} \rightarrow \omega_n^{\text{in}}$.

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.

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 100 cm\textsuperscript{-1} for plotting purposes.

We computed the phonon frequencies of P4\textsubscript{2}nnmc , Pmn2\textsubscript{1} , Pca2\textsubscript{1} , Pbca (O1), 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\textsuperscript{-1} for P4\textsubscript{2}nnmc , $\omega(A_{1g}) = 343$ cm\textsuperscript{-1} for Pca2\textsubscript{1} , $\omega(B_{2g}) = 693$ cm\textsuperscript{-1} for Pmn2\textsubscript{1} , $\omega(A_{g}) = 513$ cm\textsuperscript{-1} for Pbca (O1), $\omega(A_{g}) = 384$ cm\textsuperscript{-1} for brookite, and $\omega(A_{g}) = 496$ cm\textsuperscript{-1} for baddeleyite. We also identified the Raman signature of AFE structures as the $\omega(B_{1g}) = 784$ cm\textsuperscript{-1} peak for brookite or the $\omega(B_{1g}) = 758$ cm\textsuperscript{-1} peak for Pbca (O1). 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.

FIG. 4. Evolution of frequency difference with respect to epitaxial strain for selected modes of (a) baddeleyite, (b) P4\textsubscript{2}nnmc , (c) Pmn2\textsubscript{1} , (d) Pca2\textsubscript{1} , (e) Pbca O1, and f brookite. The star symbols in (a) and (f) are frequency differences using experimental data from Ref.19 and the triangle symbol in (b) is the frequency difference obtained using modes and frequencies from Ref.23. 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).

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Supplementary Materials: Raman and Infrared Spectroscopy For Phase Identification and Strain Calibration of HfO$_2$. 
### A. Born effective charges

| Phase      | Atoms | \( Z_{xx}^* \) | \( Z_{xy}^* \) | \( Z_{xz}^* \) | \( Z_{yx}^* \) | \( Z_{yy}^* \) | \( Z_{yz}^* \) | \( Z_{zx}^* \) | \( Z_{zy}^* \) | \( Z_{zz}^* \) | 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\(_{2}nm\)c | 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\(_{2}nm\)c 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.
| Phase     | Atoms | $Z^*_{xx}$ | $Z^*_{xy}$ | $Z^*_{xz}$ | $Z^*_{yy}$ | $Z^*_{yz}$ | $Z^*_{zx}$ | $Z^*_{zy}$ | $Z^*_zz$ | Nominal charge |
|-----------|-------|------------|------------|------------|------------|------------|------------|------------|-------------|----------------|
| 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             |
| 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             |
| 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 Pca2₁, 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 HfO₂ unit cell.
B. IR frequencies

Here we list the computed IR frequencies, their intensities and their symmetry.

| Mode | Freq (cm$^{-1}$) | IR (arb. u.) | Mode | Freq (cm$^{-1}$) | IR (arb. u.) | Mode | Freq (cm$^{-1}$) | IR (arb. u.) |
|------|-----------------|--------------|------|-----------------|--------------|------|-----------------|--------------|
| Bu   | 236             | 22.84        | Bu   | 232             | 20.07        | Bu   | 249             | 5.72         |
| Au   | 256             | 20.18        | Bu   | 311             | 64.83        | Au   | 256             | 20.18        |
| Bu   | 320             | 41.87        | Bu   | 345             | 24.74        | Bu   | 256             | 2.02         |
| Au   | 361             | 39.70        | Bu   | 405             | 40.35        | Bu   | 345             | 23.81        |
| Bu   | 370             | 7.43         | Bu   | 476             | 2.40         | Au   | 361             | 39.70        |
| Bu   | 411             | 24.29        | Bu   | 520             | 19.66        | Bu   | 400             | 49.06        |
| Au   | 499             | 12.55        | Au   | 575             | 9.21         | Au   | 411             | 24.29        |
| Bu   | 516             | 19.40        | Bu   | 741             | 14.87        | Bu   | 455             | 9.53         |
| Au   | 614             | 12.53        | Au   | 750             | 96.89        | Au   | 499             | 12.55        |
| Bu   | 651             | 76.23        | Au   | 246             | 2.62         | Au   | 614             | 12.53        |
| Bu   | 743             | 16.88        | Au   | 462             | 35.04        | Au   | 720             | 51.99        |
| Bu   | 813             | 60.68        | Au   | 627             | 39.86        | Au   | 606             | 2.84         |
| Au   | 614             | 12.53        | Au   | 432             | 3.06         | Au   | 606             | 2.84         |
| Bu   | 701             | 2.10         | Au   | 451             | 31.75        | Au   | 451             | 31.75        |
| Au   | 722             | 43.82        | B1   | 250             | 25.10        | B1   | 300             | 32.60        |
| B1   | 300             | 32.60        | A1   | 254             | 3.80         | B1   | 345             | 2.01         |
| B1   | 300             | 32.60        | B1   | 432             | 3.06         | A1   | 364             | 2.93         |
| A1   | 587             | 3.01         | A1   | 451             | 31.75        | A1   | 451             | 31.75        |
| B1   | 587             | 3.01         | B1   | 250             | 25.10        | A1   | 451             | 31.75        |
| A1   | 701             | 2.10         | B1   | 250             | 25.10        | B1   | 492             | 10.10        |
| A1   | 722             | 43.82        | B1   | 606             | 2.84         | A1   | 606             | 2.84         |
| B1   | 738             | 20.90        | B1   | 632             | 20.16        | B2   | 692             | 47.97        |

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.) | Mode | Freq (cm$^{-1}$) | IR (arb. u.) | Mode | Freq (cm$^{-1}$) | IR (arb. u.) |
|------|-----------------|--------------|------|-----------------|--------------|------|-----------------|--------------|
| Bu   | 95              | 19.57        | Bu   | 95              | 19.57        | Bu   | 95              | 19.57        |
| Au   | 95              | 19.57        | Au   | 246             | 2.62         | Au   | 246             | 2.62         |
| E_u  | 462             | 35.04        | A_{2u} | 324             | 39.86        | A_{2u} | 324             | 39.86        |
| E_u  | 462             | 35.04        | E_u  | 462             | 35.04        | E_u  | 462             | 35.04        |
| A_{2u} | 627             | 39.86        | E_u  | 720             | 51.99        | E_u  | 720             | 51.99        |

TABLE S4. Frequencies of IR-active modes for P4_{2}\text{mc}. 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.) |
|------|-----------------|--------------|------|-----------------|--------------|------|-----------------|--------------|
| B2   | 250             | 25.10        | A_1  | 177             | 6.80         | A_1  | 177             | 6.80         |
| B_1  | 300             | 32.60        | B_2  | 250             | 25.10        | B_1  | 254             | 3.80         |
| B_2  | 451             | 24.87        | B_1  | 254             | 3.80         | B_1  | 300             | 32.60        |
| B_1  | 492             | 10.10        | A_1  | 364             | 2.93         | A_1  | 254             | 3.80         |
| A_1  | 587             | 3.01         | A_1  | 364             | 2.93         | A_1  | 364             | 2.93         |
| B_1  | 701             | 2.10         | B_2  | 451             | 24.87        | B_2  | 345             | 2.01         |
| A_1  | 722             | 43.82        | B_1  | 451             | 24.87        | A_1  | 492             | 10.10        |
| B_1  | 738             | 20.90        | A_1  | 606             | 2.84         | B_1  | 606             | 2.84         |
| B_1  | 738             | 20.90        | B_1  | 632             | 20.16        | B_2  | 692             | 47.97        |

TABLE S5. Frequencies of IR-active modes for Pmn2_{1}. 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\(_1\) | 144 | 1.06 | A\(_1\) | 122 | 2.18 | A\(_1\) | 122 | 2.18 |
| B\(_1\) | 237 | 40.77 | A\(_1\) | 163 | 8.47 | B\(_1\) | 144 | 1.06 |
| B\(_1\) | 248 | 1.29 | A\(_1\) | 260 | 2.19 | A\(_1\) | 163 | 8.47 |
| B\(_2\) | 275 | 37.59 | B\(_2\) | 275 | 37.59 | B\(_1\) | 237 | 40.77 |
| B\(_2\) | 335 | 2.14 | B\(_1\) | 305 | 2.09 | B\(_1\) | 248 | 1.29 |
| B\(_2\) | 393 | 50.69 | A\(_1\) | 333 | 5.98 | A\(_1\) | 260 | 2.19 |
| B\(_1\) | 397 | 49.25 | B\(_2\) | 335 | 2.14 | A\(_1\) | 333 | 5.98 |
| A\(_1\) | 431 | 3.16 | A\(_1\) | 342 | 46.83 | A\(_1\) | 342 | 46.83 |
| B\(_2\) | 490 | 1.94 | B\(_2\) | 393 | 50.69 | B\(_1\) | 397 | 49.25 |
| B\(_1\) | 532 | 8.19 | A\(_1\) | 471 | 19.92 | A\(_1\) | 471 | 19.92 |
| A\(_1\) | 593 | 8.10 | B\(_2\) | 490 | 1.94 | B\(_1\) | 532 | 8.19 |
| B\(_2\) | 644 | 3.79 | B\(_1\) | 510 | 4.39 | A\(_1\) | 606 | 1.95 |
| A\(_1\) | 676 | 75.48 | A\(_1\) | 606 | 1.95 | B\(_2\) | 610 | 22.60 |
| B\(_1\) | 747 | 7.78 | B\(_2\) | 644 | 3.79 | B\(_2\) | 692 | 22.93 |
| B\(_1\) | 652 | 49.35 | B\(_1\) | 796 | 53.18 | B\(_1\) | 747 | 7.78 |

TABLE S6. Frequencies of IR-active modes for Pca\(_2\)_1. 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\(_{3u}\) | 477 | 7.51 | B\(_{1u}\) | 515 | 22.85 | B\(_{1u}\) | 233 | 15.82 |
| B\(_{2u}\) | 512 | 30.16 | B\(_{1u}\) | 262 | 9.72 | B\(_{3u}\) | 249 | 15.35 |
| B\(_{3u}\) | 393 | 64.30 | B\(_{2u}\) | 358 | 20.51 | B\(_{1u}\) | 262 | 9.72 |
| B\(_{3u}\) | 454 | 4.70 | B\(_{2u}\) | 386 | 64.30 | B\(_{3u}\) | 397 | 49.25 |
| B\(_{3u}\) | 477 | 7.51 | B\(_{2u}\) | 512 | 30.16 | B\(_{3u}\) | 353 | 1.43 |
| B\(_{2u}\) | 512 | 30.16 | B\(_{1u}\) | 515 | 22.85 | B\(_{3u}\) | 379 | 127.96 |
| B\(_{1u}\) | 573 | 7.54 | B\(_{2u}\) | 617 | 19.59 | B\(_{3u}\) | 454 | 4.70 |
| B\(_{2u}\) | 617 | 19.59 | B\(_{3u}\) | 653 | 154.48 | B\(_{2u}\) | 476 | 8.89 |
| B\(_{1u}\) | 623 | 73.73 | B\(_{1u}\) | 742 | 25.26 | B\(_{3u}\) | 477 | 7.51 |
| B\(_{1u}\) | 805 | 113.23 | B\(_{3u}\) | 811 | 9.98 | B\(_{2u}\) | 669 | 2.11 |
| B\(_{3u}\) | 806 | 2.00 | B\(_{1u}\) | 742 | 25.26 | B\(_{2u}\) | 742 | 184.42 |
| B\(_{3u}\) | 806 | 2.00 | B\(_{2u}\) | 742 | 184.42 | B\(_{3u}\) | 806 | 2.00 |

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 | 88.62 |
| 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$_{2u}$ | 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 |
| B$_{3u}$ | 752 | 17.74 | B$_{3u}$ | 808 | 111.77 |                            |                          |

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