Supplementary Information

Title: Fluoridation of HfO_2

Authors: Steven Flynn[1], Chi Zhang[2], Kent J. Griffith[1], Jiahong Shen[2], Christopher Wolverton[2], Vinayak P.

Dravid[2], Kenneth R. Poeppelmeier[1]*

[1] Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States
[2] Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States
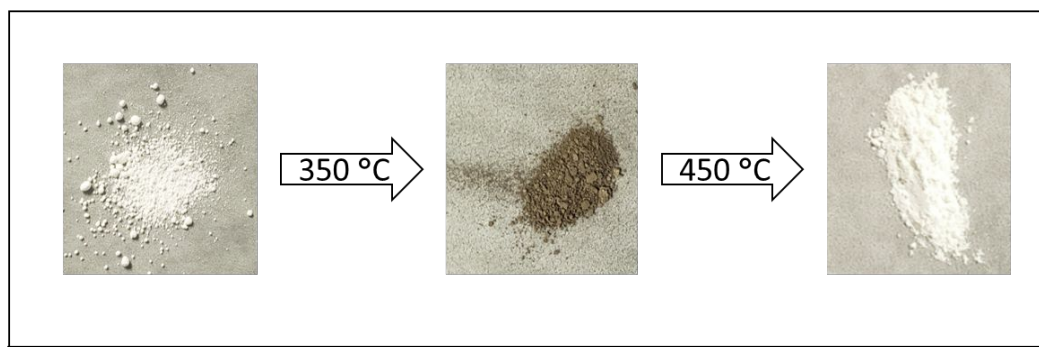
E-mail: krp@northwestern.edu

Figure S1: Color changes upon reaction of HfO_2 with PVDF. Fluoropolymer was added only to the initial reaction mixture.
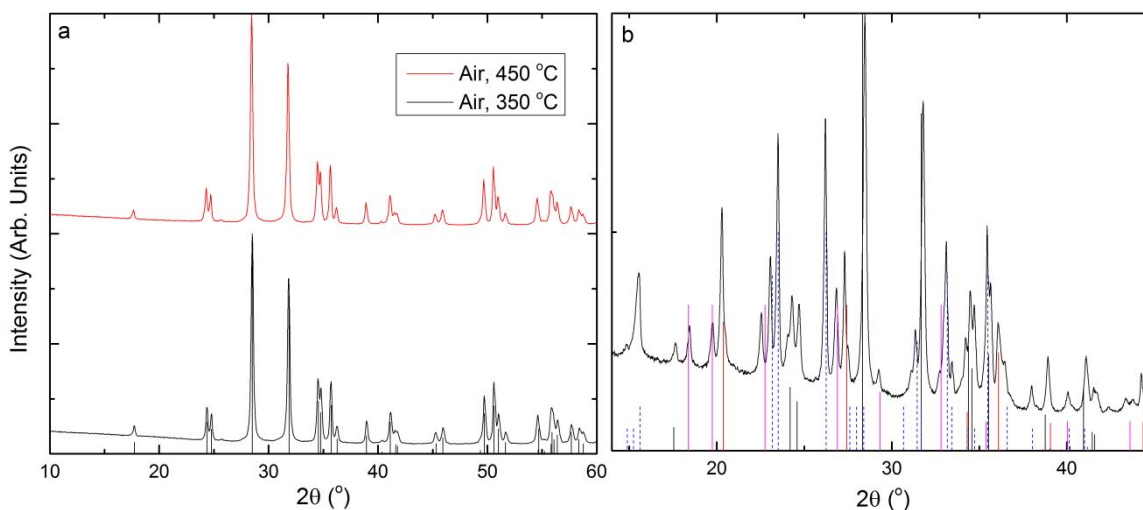

Figure S2: PXRD patterns of reaction products of HfO_2 and PVDF in (a) air and (b) an evacuated sealed tube (350 °C). Vertical lines are the reflections for known or reported phases: HfO_2 in the baddelyite structure (black), $HfSiO_4$ (red), Zr_2OF_6 (blue), and tetragonal Hf_2OF_6 (magenta). Dashed lines indicate phases reported as a list of reflections without further structural information.

In **Figure S2b**, in addition to unreacted HfO_2, which still appears to make up a majority of the product, a set of peaks matching $HfSiO_4$ is clearly present, suggesting that some reaction with the tube took place. The remaining peaks were compared to reported patterns for known fluorides and oxyfluorides of Hf and Zr. The latter phase space was included because it is has been more thoroughly investigated and the similar chemistries of Hf and Zr makes analogous compounds between the two quite likely. One set of peaks appears to be a close match for tetragonal Hf_2OF_6, (tet-Hf_2OF_6) except the (112) peak at ~22.5° which is slightly shifted from the predicted position. Rickard and Waters reported that the primary effect of hydration on the structure of this phase was to expand the *c*-axis, suggesting that water content may be responsible for this mismatch.[1] Alternatively, **Figure S3** shows that the same set of peaks can be matched to the reported pattern for $Zr_3(OH)_2F_{10}$ (PDF 00-020-1466)[2]. While no structural model has been reported for this phase, it is possible that an Hf analogue has been formed. The former phase is used to identify the product in the main text. Finally, the remaining unmatched peaks in the product pattern appear to correspond well to a reported pattern for Zr_2OF_6 (PDF-00-040-1095)[3], suggesting that this may be an unreported polymorph of the isostructural Hf analogue, Hf_2OF_6. Although a discrepancy between the predicted and actual positions is clearly apparent, it is consistent with other isostructural Hf and Zr compounds such as HfO_2 and ZrO_2, where the former is slightly contracted relative to the latter. Unfortunately, no crystallographic model has been reported in association with this powder pattern for Zr_2OF_6, so the relationship with known tet-Hf_2OF_6 structures remains unclear. This fact along with the unconfirmed composition of the unknown phase are the reasons authors only tentatively identify the new phase as "Hf_2OF_6" in the main text. Attempts to isolate this potentially new heteroanionic Hf compound via adjustment of the fluorinating agent ratio, tube size, and reaction time were unsuccessful.
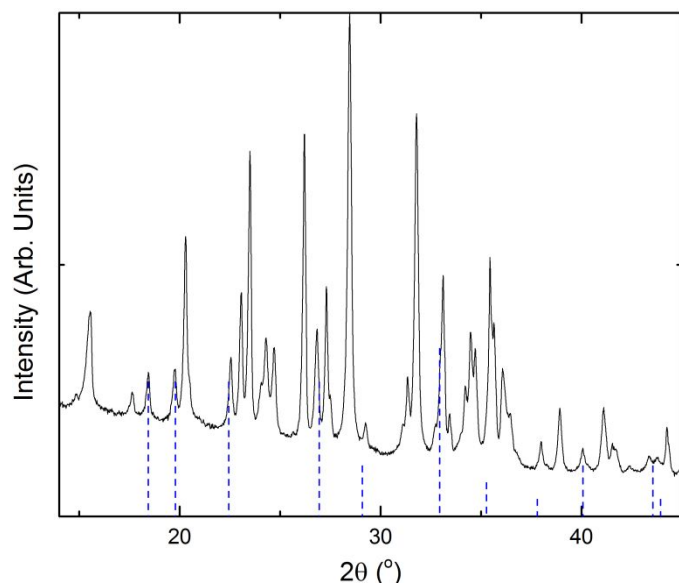
Figure S3: PXRD patterns of reaction products of HfO_2 and PVDF in an evacuated sealed tube (350 °C). Blue vertical lines are the reflections for $Zr_3(OH)_2F_{10}$[2], which is reported as a list of reflections without further structural information.
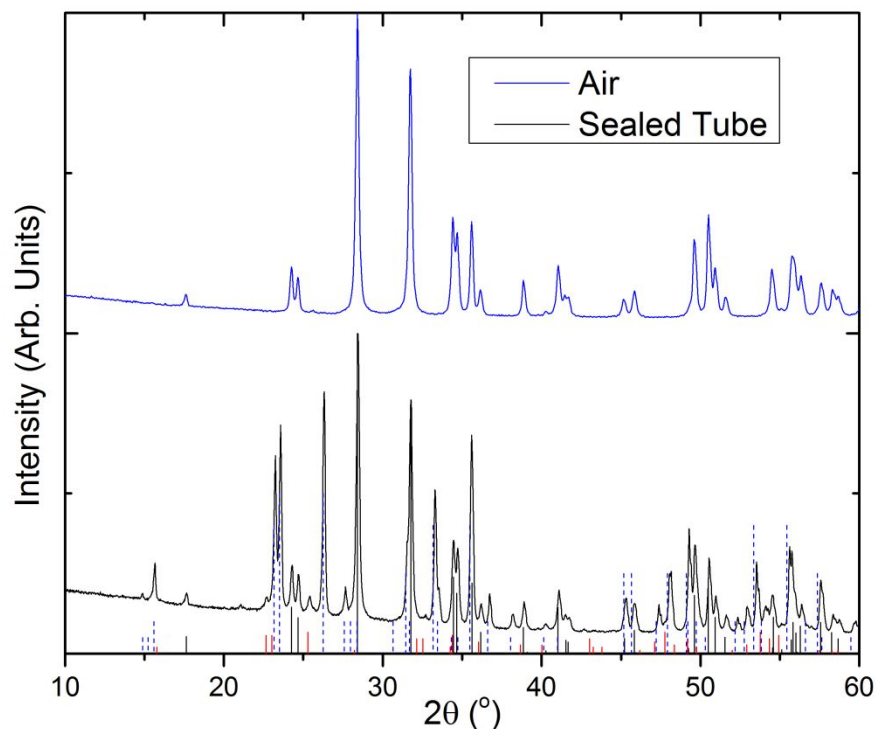

Figure S4: PXRD patterns of reaction products of HfO_2 and PTFE. Vertical lines are the predicted reflections for HfO_2 (black), α-HfF_4 (red), and Zr_2OF_6 (blue)[3]. Dashed lines indicate phases reported as a list of reflections without further structural information.

Like with the PVDF reactions, the most prominent peaks most likely indicate the presence of

HfO_2 and an unreported Hf analogue of Zr_2OF_6. Furthermore, the remaining minor peaks are best

matched by α-HfF$_4$, a fully fluorinated product. Finally, in some cases, an additional peak was observed

at ~18° with no obvious match to any known Zr or Hf oxide, fluoride, or oxyfluoride phases. However,

previous studies of fluorination with fluoropolymers have indicated the presence of extra peaks arising

from carbonaceous byproducts such as graphite fluoride.[4] As such, a control was performed under the

same conditions as the reaction but without the addition of any HfO$_2$, only PTFE. As shown **Figure S5**,

the main peak of this reaction exactly matches the unknown peak. Thus, this product appears solely

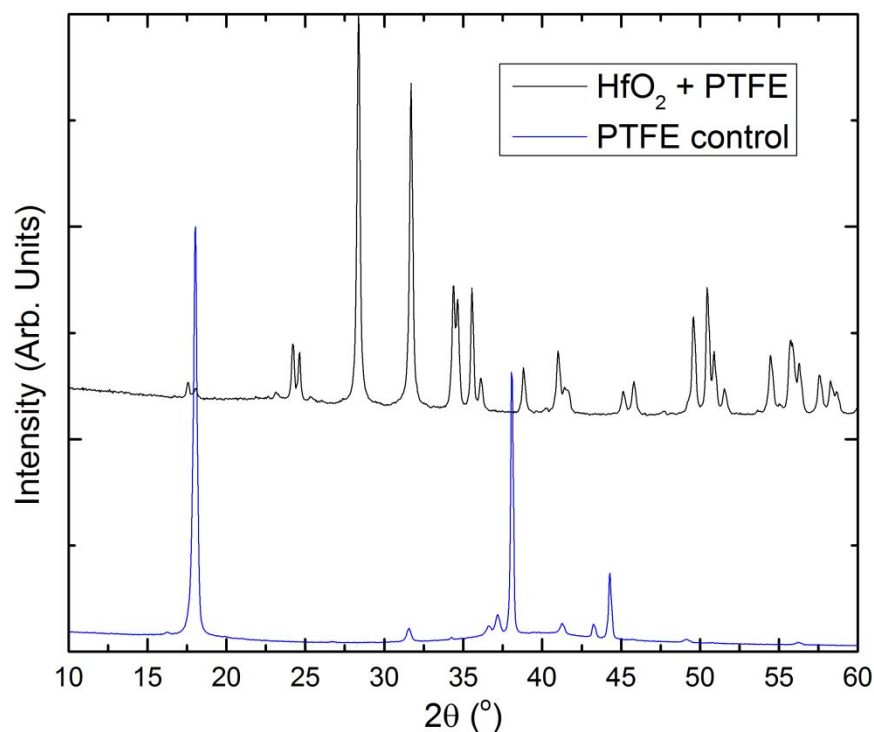attributable to the breakdown of PTFE in vacuum, and possibly with its reactions with the fused silica

tube.[5]

Figure S5: Comparison of the products of heating a small amount of PTFE at 450 °C in a sealed fused silica tube with (black) and without (blue) the presence of HfO$_2$. The most intense peaks of the latter matches the position of the only unknown peak in the former (**Figure 2**, main text).

The data in **Figure S5** appear to suggest that the phases indicated by the unknown peak at ~18° are not

new oxyfluoride phases. The lowest angle non-HfO$_2$ peak corresponds well with a pattern produced

when PTFE is heated to 450 °C in a sealed tube alone (PTFE control). This suggest that it belongs to some

carbon residue or by product of reaction with the fused silica tube. Although the other intense peaks of

this pattern are not observed in the experimental pattern, it is highly likely that the control product is

multi-phasic as a result of complex polymer degradation mechanisms, and that in the presence of

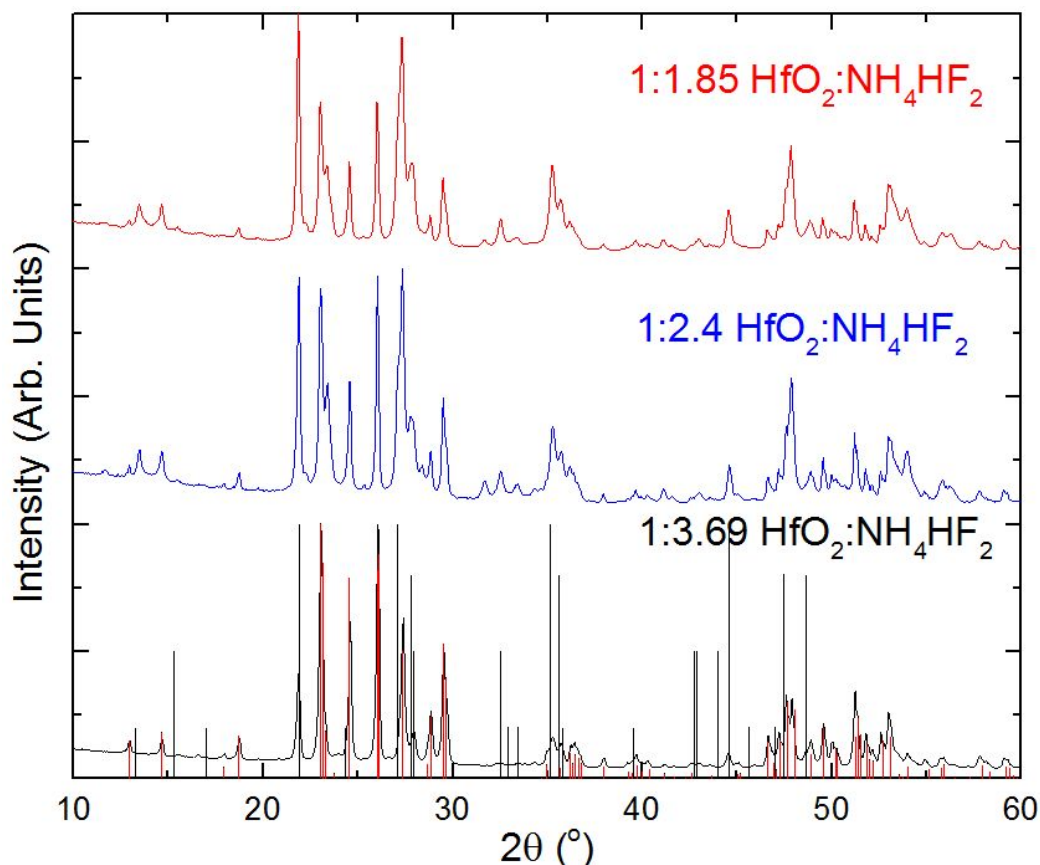additional material not all of them remain unreacted.

Figure S6: PXRD patterns of the reaction products of HfO_2 and NH_4HF_2 at three different molar ratios. Vertical lines indicate theoretical peak positions for β-HfF_4 (red) and $Zr_7O_9F_{10}$ (black). The shaded region indicates one easily-distinguished high intensity peak from each phase. The relative intensities of these peaks reverses as the reactant ratio is varied from 1:3.69 to 1:1.85 (HfO_2:NH_4HF_2).
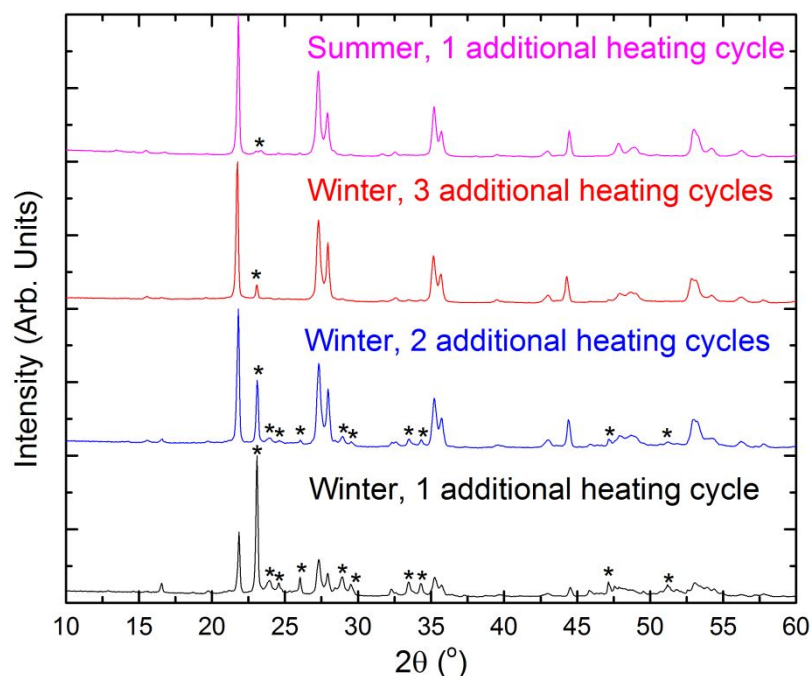
Figure S7: PXRD patterns of the reaction products of HfO_2 and NH_4HF_2 after 1-3 additional heating cycles in different seasons (and therefore different ambient humidities). Asterisks mark prominent β-HfF_4 peaks.

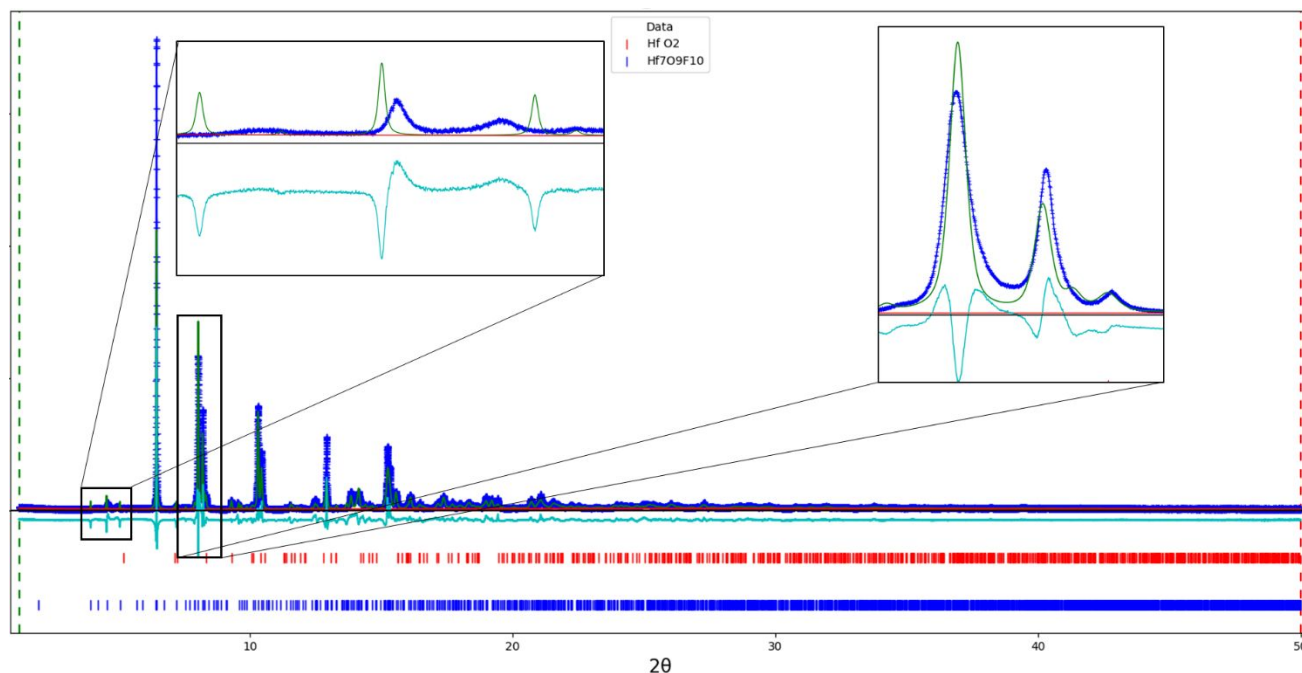**Figure S8:** Rietveld refinement of synchrotron diffraction data of the new hafnium oxyfluoride phase, wR = 26.409%. (Inset) Zoom-in views of areas of disagreement between refined model and experimental data. (Blue) Observed powder pattern. (Green) Calculated powder pattern. (Light blue) Difference.
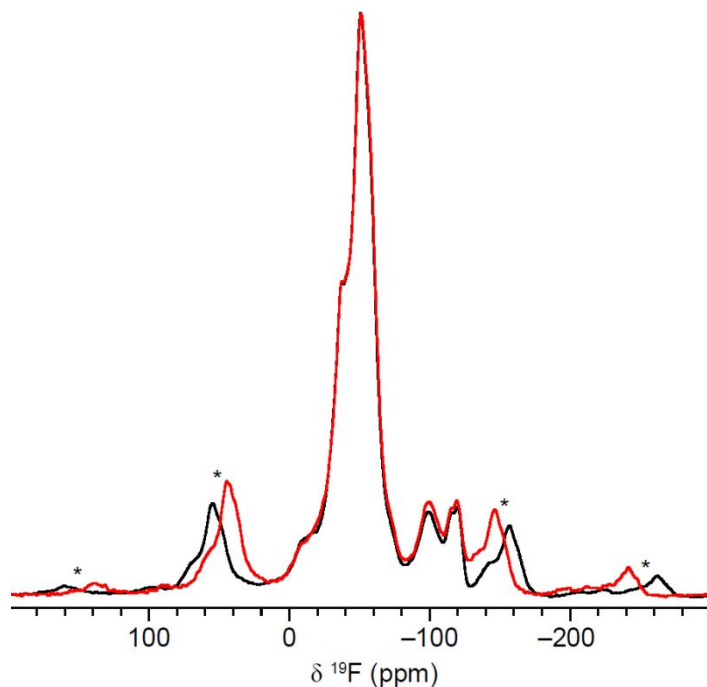
Figure S9: Comparison of ^{19}F NMR of the unknown Hf-O-F phase at 40 (black) and 36 (red) kHz MAS. Peaks that do not shift represent isotropic resonances. Spinning sidebands are denoted with asterisks.

Table S1: Spectral parameters used to fit the ^{19}F NMR spectrum of the hafnium oxyfluoride sample in **Figure 2** in the main text.[a]

	δ_{iso} [±0.1] (ppm)	δ_{CSA} [±10] (ppm)	η_{CSA} [±0.2]	Relative Intensity
1	–13.5	–140	0.5	0.04
2	–37.0	–108	0.7	0.22
3	–51.2	–140	0.4	0.50
4	–59.5	–125	0.1	0.11
5	–99.4	–80	0.1	0.08
6	–115.3	–140	0.05	0.03
7	–120.0	–100	0.1	0.01

[a]In this work, the Haeberlen convention is adopted to describe the chemical shift tensor. In this convention, the isotropic shift δ_{iso} is given by $\delta_{iso} = \frac{\delta_{XX} + \delta_{YY} + \delta_{ZZ}}{3}$ with the chemical shift anisotropy δ_{CSA} defined as $\delta_{CSA} = \delta_{ZZ} - \delta_{iso}$ and the shift asymmetry η_{CSA} defined as $\eta_{CSA} = \frac{\delta_{YY} - \delta_{XX}}{\delta_{ZZ} - \delta_{iso}}$. Within these definitions, the principal components of the shift tensor are ordered such that $|\delta_{ZZ}-\delta_{iso}| \geq |\delta_{XX}-\delta_{iso}| \geq |\delta_{YY}-\delta_{iso}|$. *N.b.* This definition of δ_{CSA} is sometimes referred to as the reduced anisotropy, which is equal to 2/3 of the 'full' anisotropy $\Delta\delta = \delta_{ZZ} - \frac{\delta_{XX} + \delta_{YY}}{2}$ used by some authors and programs.
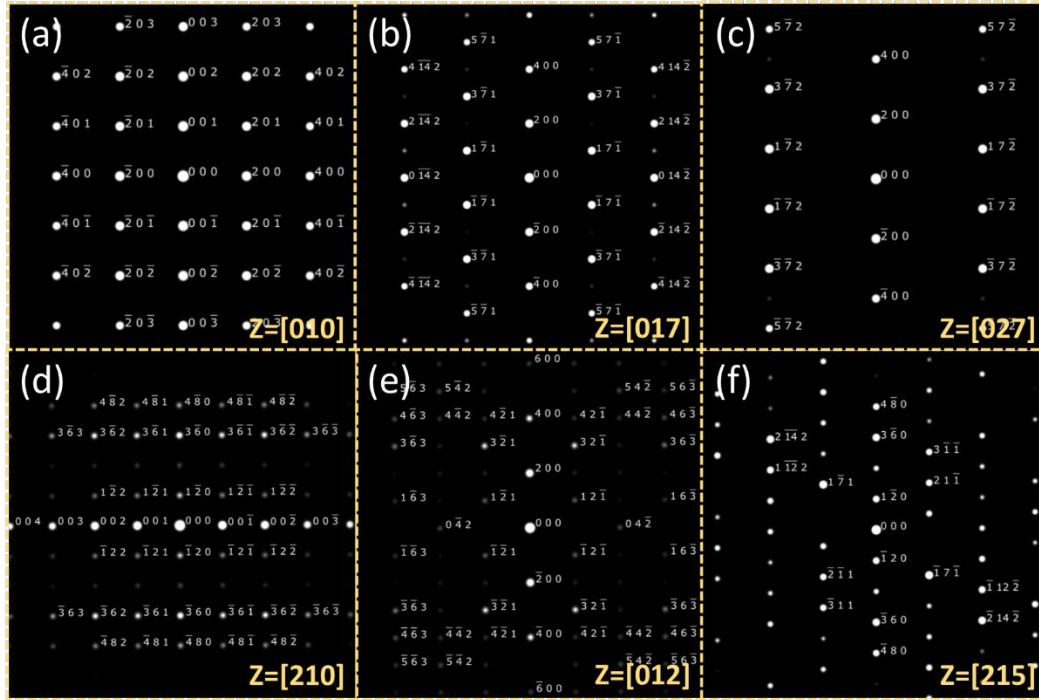
Figure S10: Simulated SAED patterns of [010] (a), [017] (b), [027] (c), [210] (d), [012] (e) and [215] (f) zone axes of the Hf-O-F sample based on hypothetical model with lattice parameters from Rietveld refinement.

Table S2: Parameters for the improved Rietveld refinement of the hypothetical "$Hf_7O_9F_{10}$" structure.

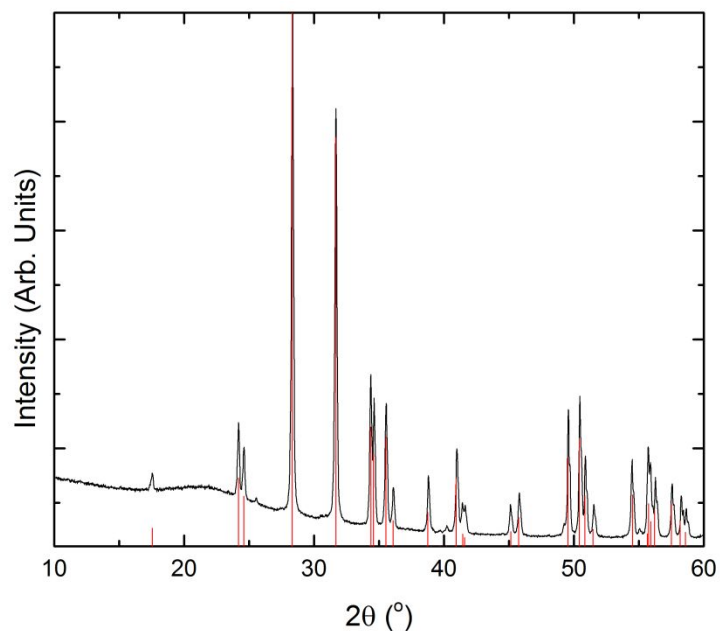| Source	Synchrotron
Chemical Formula	$Hf_7O_9F_{10}$
Formula Weight	1583.41
Temperature (K)	295
Wavelength (Å)	0.457927
Crystal System	Orthorhombic
Space group (No.)	Pbam (55)
a (Å)	6.3965(3)
b (Å)	26.5759(11)
c (Å)	4.06843(15)
$\alpha = \beta = \gamma$ (deg)	90
V (Å^3)	691.61(8)
Z	1
Profile range	$0.5 \leq 2\theta \leq 50$
GOF	3.45
R_p (%)	13.82
R_{wp} (%)	18.26

Figure S11: PXRD of bulk hafnium oxyfluoride produced by reaction of HfO_2 with NH_4HF_2 after thermal analysis (TGA). Sample was heated at 10 °C/min to 800 °C in He atmosphere, held there for 30 minutes and cooled at the same rate. Red vertical lines indicate theoretical reflections for HfO_2. Low sample quantity (~30 mg) resulted in an incompletely covered glass PXRD slide, producing the observed amorphous background.
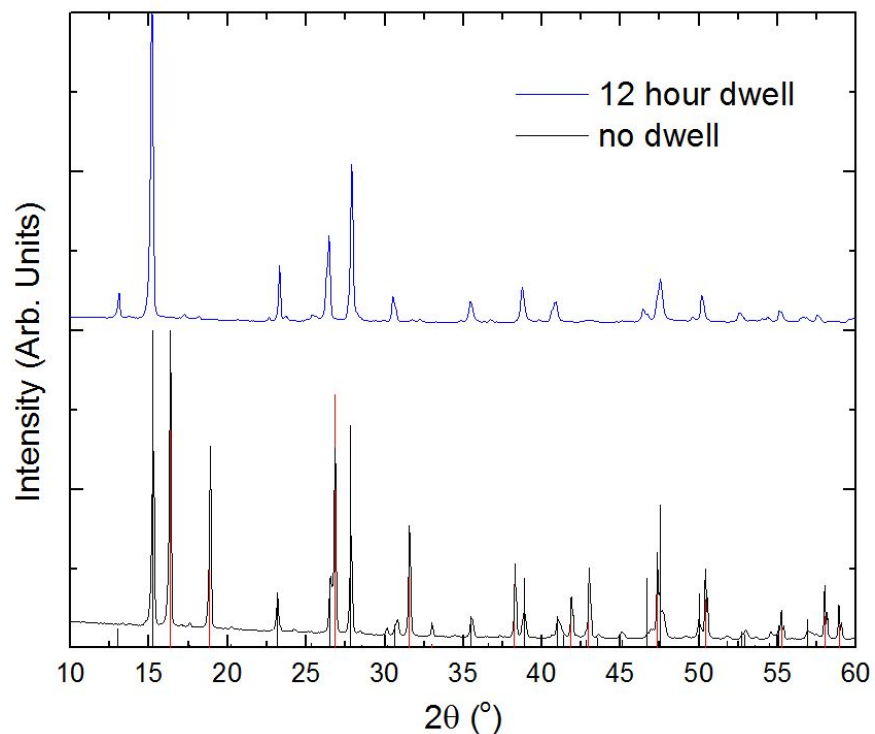

Figure S12: PXRD of the product of a mixture of HfO_2 and NH_4HF_2 in 1:3.5 molar ratio after reaction at 250 °C in air for 12 hours. Vertical lines indicate the predicted peak positions for $(NH_4)_2HfF_6$ (black) and $(NH_4)_3HfF_7$ (red).
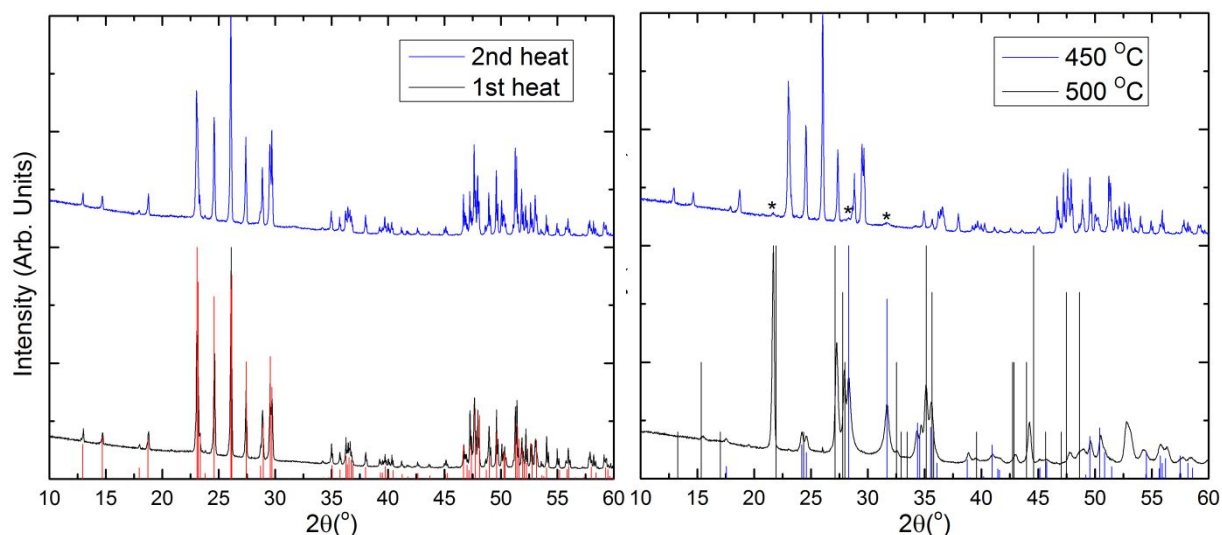
Figure S13: PXRD of well-ground, commercial HfF_4 after heating in a covered Al_2O_3 crucible air. (left) successive cycles of heating to 420 °C and dwelling for 12 hours. (right) High temperature heating cycles. Asterisks indicated positions of minor secondary phases. Vertical lines indicate predicted reflections for β-HfF_4 (red), HfO_2 (blue), and $Zr_7O_9F_{10}$ (black).

References:
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3. Papiernik, R., Frit, B., Gaudreau, B. Les phases solides du système ZrO_2-ZrF_4. *Rev. Chim. Miner., 23*, **1986**, 400-436.
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5. Monnahela, O. S.; Vilakazi, B. M.; Wagener, J. B.; Roodt, A.; Carstens, P. A. B.; Retief, W. L. A Thermogravimetric Study of the Fluorination of Zirconium and Hafnium Oxides with Fluorine Gas. *J. Fluor. Chem.* **2012**, *135*, 246–249.