Kinetically stabilized ferroelectricity in bulk single-crystalline HfO$_2$:Y

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HfO$_2$, a simple binary oxide, exhibits ultra-scalable ferroelectricity integrable into silicon technology. This material has a polymorphic nature, with the polar orthorhombic (Pbc2$_1$) form in ultrathin films regarded as the plausible cause of ferroelectricity but thought not to be attainable in bulk crystals. Here, using a state-of-the-art laser-diode-heated floating zone technique, we report the Pbc2$_1$ phase and ferroelectricity in bulk single-crystalline HfO$_2$:Y as well as the presence of the antipolar Pbca$_2$ phase at different Y concentrations. Neutron diffraction and atomic imaging demonstrate (anti)polar crystallographic signatures and abundant 90°/180° ferroelectric domains in addition to switchable polarization with negligible wake-up effects. Density-functional-theory calculations indicate that the yttrium doping and rapid cooling are the key factors for stabilization of the desired phase in bulk. Our observations provide insights into the polymorphic nature and phase control of HfO$_2$, remove the upper size limit for ferroelectricity and suggest directions towards next-generation ferroelectric devices.

In a quantum leap for the miniaturization of semiconductor circuits, hafnium-based high-k dielectrics have been implemented as an alternative to thin silicon dioxide gate insulators in silicon technology since 2007 (refs. 1–4). The continued dimensional scaling-down led to the observation of unexpected ferroelectricity (FE) in ultrathin HfO$_2$ films in both pure and doped forms$^{5,6}$. Their good CMOS-compatibility, as well as the robust ferroelectricity down to few layers$^6$, has strongly suggested hafnia as a promising candidate for the next generation of non-volatile memory devices beyond PZT-based ferroelectrics$^{7,8}$. In parallel, the application of hafnia-based ferroelectrics as gate insulators into negative capacitance transistors offers an avenue for extending Moore’s law$^{9,10}$.

In light of the extensive research on this relatively simple binary oxide over the past few decades, the first observation of ferroelectricity in HfO$_2$:Si thin films at room temperature was totally unexpected$^6$. The six known equilibrium phases of hafnia are all non-polar and hence incapable of supporting ferroelectricity$^{11}$. These six phases include the room temperature monoclinic ($m$) P2$_1$/c phase, the high-temperature tetragonal ($t$) P4$_2$/nmc and cubic ($c$) Fm-3m phases, and the high-pressure fluorite CaF$_2$-type antipolar orthorhombic Pbca$_2$ (o-AP) or o-I, disordered Pbem (o-DO) and the cotunnite (PbCl$_2$)-type Pmn$_2$b (o-II) phase. The results of previous computational and empirical investigations hinted at the non-equilibrium polar orthorhombic Pca$_2$$_1$ (o-FE) phase as the plausible root cause of the observed ferroelectricity in hafnia$^{11}$; however, different phases, as well as to many unexplored metastable phases, have also been experimentally identified$^{16,18}$. Perplexities and confusions arise primarily from the polymorphic nature of hafnia and also from to the challenges associated with the characterization of the mixed/complex phases in ultrathin films at small length scales$^{19}$. The different sets of growth conditions, including dopant species$^{16,20,22}$, substrates$^{16,23,25}$ and capping electrodes$^{26,27}$, all add some degree of uncertainty in these characterizations. Furthermore, various extrinsic factors such as stress$^{27}$, oxygen vacancies$^{28,30}$, surface energy$^{31}$ and electric fields$^{32}$ have been put forward to provide a rationale for the ferroelectricity$^{33}$.

Pristine ferroelectricity has been reported in 15-nm 7% HfO$_2$:Y epitaxial films$^7$, indicating the single-crystal o-FE phase could exist in the HfO$_2$:Y system. Moreover, recent findings about 1-µm-thick HfO$_2$:Y ferroelectric films, both polycrystalline and epitaxial$^{34,35}$, shed light on the thickness-independent o-FE phase. On the other hand, there are numerous reports suggesting the polarization degrades in thicker ferroelectric HfO$_2$ films, with Y or other dopants$^{30}$ and a small-size-driven $t$ to o-FE phase transition at the nanoscale has been suggested to be essential to stabilize the o-FE phase in ultrathin films$^{36}$, which is unlikely to happen in bulk crystals. Even though the o-FE phase was first reported in bulk polycrystalline Mg-doped ZrO$_2$ at 30 K (ref. 40), it was presumed not to be stable at ambient pressure and room temperature in bulk hafnia$^{11,33,41}$. Therefore, whether it is possible to grow o-FE phase large-size single crystals is still an important and challenging question.

Here, we demonstrate metastable o-FE phase and ferroelectricity at room temperature in bulk HfO$_2$:Y single crystals, which are grown using a state-of-the-art laser-diode-heated floating zone (LDFZ) technique. A comprehensive structural study using aberration-corrected scanning transmission electron microscopy (STEM) and dark-field (DF)–TEM technique exhibits the presence of abundant 90°/180° ferroelectric domains in addition, with different doping concentrations, we are able to stabilize another antipolar orthorhombic o-AP phase at room temperature and ambient pressure. The ferroelectricity in bulk crystals accompanies a negligible wake-up effect, while it is commonly observed in ultrathin films. Our results provide an essential stepping stone toward the scientific understanding of the multiplicity of (doped) hafnia towards future hafnia-based science and technologies.

Growth and structural characterization of bulk HfO$_2$:Y

To stabilize the metastable phases in bulk, whose appearance cannot be anticipated from the traditional phase diagrams, non-equilibrium...
growth through a quenching process is the key. An LDFZ furnace has the merit of well-focused laser diodes as heating sources, resulting in a high maximum temperature around 3,000 °C and a steep temperature gradient at the growth interface that enables a much higher quenching rate than the conventional infrared-lamp floating zone technique. Figure 1a shows the X-ray diffraction pattern (XRD) for pristine HfO₂:Y crystals with different yttrium doping concentrations. As revealed, the ground state of non-doped HfO₂ crystal is monoclinic and Y-rich ends in the cubic phase, similar to the famous yttrium-stabilized zirconia. New peaks appear (at 2θ = 35°, 43.5° and 75°) within the 8–12% Y doping while they disappear after a 1,600 °C annealing, indicating the meta-stability of the new phases (Supplementary Fig. 1). Twelve percent HfO₂:Y is particularly interesting as the monoclinic phase is fully suppressed, accompanying the disappearance of (111)₀ and (111)₉ reflections at 2θ = 28.5° and 31.7° (Fig. 1a). The profile fitting leads to tetragonal/orthorhombic unit cells with aspect ratio c/a or 2b/(a + c) ≅ 1.01 and possible candidates for the t, o-AP, o-DO or o-FE phases. The similarity comes that o-AP can be considered alternate stacks of o-FE domains and resulting in the a-lattice doubling while the o-DO can be treated as a macroscopic average of o-FE domains.

A representative crystal image of 12% HfO₂:Y is displayed in Fig. 1b. A HfO₂:Y transparent crystal boule up to 50 mm long can be grown. A transmission polarized optical microscope (tPOM, shown in Fig. 1c) reveals a tweed texture on a cutting surface, namely a crisscross of needle-like domains, which is typical in orthorhombic
systems with fine orthorhombic twins. The twin character can be recognized in the fact that domain contrast reversal by manipulating the analyser under a tPOM. We notice 8–12% HfO2:Y crystals share some general features of tweed textures but whose details can vary (Supplementary Fig. 2). The orthogonal nature of the tweed textures is further confirmed by selected area electron diffraction (SAED) patterns under TEM (Fig. 1e–g), which rule out the presence of the t phase. The cell-doubling superlattice peaks, that is o-AP, persist in the 8–11% range, which can be clearly identified through a sequence of SAED patterns (Fig. 1e and Supplementary Fig. 3), whereas they disappear in the 12% HfO2:Y crystal (Fig. 1f and Supplementary Fig. 4). A closer examination of those SAED patterns in the 12% HfO2:Y crystal reveals no peak splitting or diffuse streaking attributing to the formation of mixed phases or defects. Although the same extinction rules in polymorph o-DO and o-Fe yield ambiguity to distinguish them in 12% HfO2:Y using three-dimensional SAEDs; instead, neutron scattering is the solution and notably, it is recognized in the fact that domain contrast reversal by manipulating the polar axes as indicated by white tweeds occur because of the different thermal histories.

**o-Fe neutron refinement**

Next, the o-Fe phase of 12% HfO2:Y is determined by a series of single- or multi-phase Rietveld refinements of neutron powder diffraction (NPD) patterns. The use of a neutron that penetrates mass to the extent of 12% HfO2:Y using three-dimensional SAEDs; instead, neutron scattering is the solution and notably, it is recognized in the fact that domain contrast reversal by manipulating the polar axes as indicated by white tweeds occur because of the different thermal histories.

**Ferroelectricity and 90°/180° ferroelectric domains**

The bulk orthorhombicity, which is defined by \(\varepsilon = \frac{(c-a)}{(c+a)} \times 100\% = 0.017\%\) in the present work, is about six times smaller than the reported value 0.099% in the HfO2:Gd thin film. The small orthorhombicity explains in part the tweed textures observed in the tPOM (Fig. 1c) and DF–TEM images along [010]_o-FE (Supplementary Fig. 5). Those fine ac tweeds occur because of the ferroelectric spontaneous strain and are characterized by a cross-hatching of up to a few hundred nanometres in length. The atomically resolved positions of the projected Hf atom sublattice and the tweed boundary are readily determined using high-angle annular dark-field (HAADF)–STEM that displays strong contrast associated with the heavy Hf atoms (Fig. 3a,b). Figure 3c,d indicates a 90° rotation of the diffractograms by fast Fourier transform (FFT) operations of green and red selected areas in Fig. 3a. In real space, the periodic short-long Hf–Hf bonding along the a axis revealed by overlaid colour-coded o-Fe unit cells also rotates 90° across the tweed boundary oriented along [101]_o-FE. Since the polarization is along the c axis, these ac tweed walls are 90°-type FE domain walls. Consequently, the microstructures perpendicular to [100]_o-FE, that is [100]_o-AP and [001]_o-FE are similar, with abundant irregular-shaped ab and bc twin domains within a few hundred nanometres in size (Supplementary Fig. 5). There is an almost equal distribution of ab and bc domains. A further zoom-in HAADF–STEM image of one ab/bc twin wall (Fig. 3b) shows an atomically coherent wall along the longest b axis. The crystallographic orientation of ab/bc domains is confirmed by the diffractograms of purple and blue selected areas (Fig. 3e,f) by FFT operations. Inside those ferroelastic ac/ab/bc domains, there exist 180°-type FE domains on a 100-nm scale or less. Figure 3g,h display the DF–TEM images of FE domains with bright and grey contrasts viewing along the [111]_o-FE direction, resulting from the non-equal diffraction intensity due to the broken space-inversion of the o-Fe phase. The domains with two different contrasts are associated with the ±c polar axes as indicated by white arrows. The yellow arrows mark the ferroelastic domain walls, in which the contrast remains very dark when ±c = (112) spots were excited (Fig. 3g,b). Our DF–TEM images demonstrate consistently the presence of 180° and 90° FE domains.

Figure 3i shows polarization versus an electric-field (\(P–E\)) hysteresis loop of a pristine [100]/[001]_o-FE oriented 12% HfO2:Y crystal at room temperature, revealing a remnant polarization \(2P_r = 6\mu Cm^{-2}\) and coercive field \(E_c = 4 MV cm^{-2}\). Generally, 90° switching of ferroelectric domains has higher energy barriers compared to 180° switching. In addition, zero remnant polarization was observed when measuring along [010]_o-AP, which strongly suggests that 90° switching does not occur here. Therefore, due to abundant 90° ac twinning domains, only 50% of the total polarization can be detected when measuring along [100]/[001]_o-FE. On the basis of this assumption, the total \(2P_r\) is estimated to be 12\(\mu Cm^{-2}\). Compared with previous studies that showed \(P_r\), values 45\(\mu Cm^{-2}\), 14–17\(\mu Cm^{-2}\) and 5\(\mu Cm^{-2}\) of 15 nm epitaxial, 10–930\(\mu Cm^{-2}\) polycrystalline and 1\(\mu m\) epitaxial 7% HfO2:Y films\(^{31–37}\), respectively, our \(P_r\) value is on the same order of magnitude as the 1-\(\mu m\) epitaxial 7% HfO2:Y films. The \(E_c\) here seems larger than the reported \(E_r\) for those films (2 MV cm\(^{-2}\)), but it may not reflect the intrinsic difference since \(D–E\) loops generally give smaller \(E_r\) values than \(P–E\) loops.

Wake-up effects refer to the remnant polarization increasing or current loop shape changing after electric-field cycles, and have

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**Table 1: The structure parameters of 12% HfO2:Y from elastic neutron diffraction performed at room temperature (290 K)**

| Parameter | Value | Parameter | Value | Parameter | Value | Parameter | Value | Parameter | Value | Parameter | Value |
|-----------|-------|-----------|-------|-----------|-------|-----------|-------|-----------|-------|-----------|-------|
| \(a (\AA)\) | 5.1019(3) | \(b (\AA)\) | 5.1540(5) | \(c (\AA)\) | 5.1036(4) | Atom | Hf | \(x\) | 0.0003(9) | \(y\) | 0.2620(1) | \(z\) | 0.1926(4) | Occupancy | 0.881(6) |
|           |       |           |       |           |       | O1 | 0.2223(2) | 0.0301(9) | 0.9231(4) | 0.997(1) | 0.0537(9) |
|           |       |           |       |           |       | O2 | 0.2490(6) | 0.4928(6) | 0.4451(3) | 0.952(2) | 0.0243(8) |
|           |       |           |       |           |       | Y  | 0.0003(9) | 0.2620(1) | 0.1926(4) | 0.118(4) | 0.0143(3) |

Refined by 100% Pb2 (\(g = 15.08\%\)). \(U_{iso}\) is the isotropic displacement parameter.
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Fig. 2 | Neutron diffraction studies reveal o-FE phase of the 12% HfO₂-Y single crystal. a, Representative neutron diffraction pattern plotted against momentum transfer $Q$ (Å$^{-1}$) = 2π/d at room temperature. The red profile to the black data points is a fit to the o-FE (Pbc₂) structure. Green vertical bars indicate Bragg peak positions and the lower blue curve shows the difference between the fit and the data. b, Detail of the (220) peaks, the peaks with the strongest intensity, showing a good fit with the o-FE structure. c, Zoomed-in region showing several of the weak reflections disallowed in the tetragonal t (blue curve, $P4_{1}/nmc$ and with lower calculated intensities in the disordered o-DO (green curve, Pbcm). Those peaks could be well described by o-FE (red curve). d, Zoomed-in region of c along with refined models and hk0 indices below.

Theoretical $P$ value and wake-up effect

The measured value of the polarization is much smaller than the theoretical value for a non-doped bulk o-FE HfO₂ (61 μC cm$^{-2}$ given by the DFT calculation with the Berry phase method). This is consistent with the experimentally determined structure (Table 1), as the polarization calculated for this structure from DFT is only 9 μC cm$^{-2}$, which matches fairly well with the experimental result (6 μC cm$^{-2}$). The suppression of polar distortion can be understood as resulting from Y substitution with associated charge-compensating oxygen vacancies. In DFT calculations, we start with the pristine o-FE HfO₂ structure, introduce 12.5% Y doping and 3.25% oxygen vacancies. In DFT calculations, the clear thermal hysteresis during warming and cooling cycles is the characteristic of a first-order phase transition.

$T_c = 450°C$ has been observed in 15 nm epitaxial 7% HfO₂-Y films$^{35}$. Recently, a study on HfO₂-Y films with various thickness revealed that thicker films tend to have higher $T_c$ and 550°C has been achieved in 1-μm-thick films$^{47}$. In this sense, $T_c \approx 850°C$ for bulk crystals is in agreement with the observed trend, while an orthorhombic to cubic, instead of tetragonal, transition is found distinct from what has reported in HfO₂-Si and HfO₂-Y thin films$^{48}$.

Generally, the ferroelectricity always accompanies a well-defined Curie temperature ($T_c$). In Supplementary Fig. 7, the o-FE to cubic Curie transition at $T_c \approx 800 ± 50°C$ is demonstrated using in situ heating TEM. The clear thermal hysteresis during warming and cooling cycles is the characteristic of a first-order phase transition.

been widely observed in HfO₂-based ferroelectric films. The first ten positive up, negative down (PUND) measurements are performed on another [100]/[001]o-FE piece of pristine 12% HfO₂:Y crystal to test possible wake-up effects. The resultant remnant polarizations on another [100]/[001]o-FE piece of pristine 12% HfO₂:Y crystal to avoid sample breakdown. Nevertheless, 4.67 MV cm$^{-1}$ is still higher than the coercive field 4 MV cm$^{-1}$, thus is supposed to be enough to activate wake-up effects, if there are any. Figure 3j and coercive fields are presented in Fig. 3j, and all whole loops test possible wake-up effects. The resultant remnant polarizations after applying a series of 10,000 Hz and 4.67 MV cm$^{-1}$ pulses for 1 s are shown in Supplementary Fig. 6. Note that the maximum electric field used in the wake-up test (4.67 MV cm$^{-1}$) is slightly lower than the maximum electric field used in Fig. 3i (5.93 MV cm$^{-1}$) to avoid sample breakdown. Nevertheless, 4.67 MV cm$^{-1}$ is still higher than the coercive field 4 MV cm$^{-1}$, thus is supposed to be enough to activate wake-up effects, if there are any. Figure 3j reveals that 2P is enhanced by 15% (4.68 to 5.38 μC cm$^{-2}$) and $E_c$ slightly increases from 3.69 to 3.79 MV cm$^{-1}$ in the first three loops. Afterwards, both $P_r$ and $E_c$ do not show measurable change even after applying a series of 10,000 Hz and 4.67 MV cm$^{-1}$ pulses for 1 s (Supplementary Fig. 6). The change of polarization is negligible compared with typically reported wake-up effects in HfO₂-based ferroelectric films$^{46}$. 

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Fig. 8), indicating the robustness of the DFT method. We find that the optimized structure exhibits a polar distortion \( Q_p \) of only 0.015 Å (see Supplementary Fig. 9 for the definition of \( Q_p \)), which is in the same order of magnitude of the experimental result 0.035 Å (for comparison, the value for non-doped \( \alpha \)-FE HfO\(_2\) is 0.235 Å).

Furthermore, the reported polarization values in several HfO\(_2\):Y thin films are also small (roughly 5 \( \mu \)C cm\(^{-2}\))\(^{37,49}\), which further supports our point.

Generally, the wake-up effect originates from two mechanisms: (1) the elimination of internal bias induced by the redistribution...
of oxygen vacancies\(^{40,51}\) and (2) the non-polar to polar phase transition\(^{18,25}\). However, neither of them applies to our case. Our bulk HfO\(_2\) does not have interfaces where oxygen vacancies concentrate. The oxygen vacancies are distributed in association with the substituted Y, and the fast quenching also tends to prevent the diffusion of oxygen vacancies. As a result, our sample is unlikely to possess any particular region pinned by a high oxygen vacancy concentration. Moreover, our bulk sample adopts a pristine o-FE phase and does not have any electric field-induced non-polar to polar phase transition.

**Discussion about growth and kinetic theory**

In contrast to the present work, degrading orthorhombic phase portion and ferroelectricity with increasing thickness has been widely observed in HfO\(_2\)-based films\(^{38}\), which is possibly due to strain relaxation and phase separation. The bulk crystal growth technique provides an alternative to overcome those bottlenecks. HfO\(_2\)-Y solid solution with a uniform yttrium distribution crystallizes from a molten liquid at temperatures above 2,700°C. After a subsequent rapid cooling, the yttrium diffusion is frozen resulting in a supersaturation state. The huge chemical pressure from yttrium supersaturation certainly drives the formation of metastable orthorhombic phases. The 1,600°C annealing on pristine HfO\(_2\)-Y crystals results in the decomposition of the orthorhombic phase into cubic and monoclinic phases (Supplementary Fig. 1), probably because the yttrium diffusion is activated again at 1,600°C. Annealing with moderate temperatures such as 1,000°C does not change the phase.

![Fig. 4 Energy landscape and barriers of representative transformation paths from DFT calculations.](image)

Table 2 The energy barriers \(\Delta E\) of the representative transformation paths shown in Fig. 4, with and without the lattice constants

| Number of the path | 1   | 2   | 3   | 4   | 5   |
|-------------------|-----|-----|-----|-----|-----|
| Phase transitions | \(t \rightarrow o\)-FE | \(t \rightarrow o\)-FE | \(t \rightarrow o\)-AP | \(t \rightarrow o\)-AP | \(t \rightarrow m\) |
| \(\Delta E\) (lattices unfixed) | 46.0 | 46.0 | 72.8 | 68.8 | 50.4 |
| \(\Delta E\) (lattices fixed) | 60.0 | 54.0 | 105.9 | 90.3 | 360.4 |

The unit of energy is meV per formula unit. Refer to Supplementary Fig. 10 for the energy profiles of HfO\(_2\) with lattice constants fixed.

Specifically, our DFT calculations demonstrate that the bulk \(o\)-FE HfO\(_2\) phase can be kinetically stabilized by the joint effect of quenching and yttrium supersaturation. In Fig. 4a, we plot the energy landscape of bulk HfO\(_2\) as a function of the amplitudes of several characteristic modes (see Supplementary Fig. 9 for the definitions and detailed descriptions of these modes). The energy landscape contains several local minima, which corresponds to the stable or metastable \(t\), \(m\), \(o\)-AP and \(o\)-FE phases. Here, instead of the \(c\) phase, the \(t\) phase is viewed as the high-temperature phase, since the \(c\) phase is unstable in DFT calculation (\(T = 0\) K) and automatically collapses to the \(t\) phase\(^{11,12}\). This assumption is reasonable since the \(t\) and \(c\) phases share similar physical properties\(^{11,12}\). Note that no hint of the \(t\) phase is detected in the in situ heating TEM experiment (Supplementary Fig. 7).

The energy profiles of several representative transformation paths linking the high-temperature \(t\) phase and three different low-temperature phases (\(m\), \(o\)-AP and \(o\)-FE) are shown in Fig. 4b. Our DFT calculations reveal that even though the \(o\)-FE phase has the highest energy among the low-temperature phases, the \(t\) to \(o\)-FE phase transition has the smallest energy barrier. Fast cooling (quenching) makes the transformation path with a smaller energy barrier more favourable. The necessity of the kinetic model is illustrated in more detail in the Supplementary Discussion and Supplementary Fig. 11. Moreover, supersaturated Yttrium increases the ratio of the interface boundary area of the new phase nuclei during cooling\(^{34}\). To reduce the strain energy, the nuclei tend to have similar lattice constants as the parent \(t\) phase. We carry out DFT calculations to obtain the energy barriers of the representative paths shown in Fig. 4, but with the fixed lattice constants as in the \(t\) phase. Our results, listed in Table 2, clearly show that the energy barriers are enlarged and \(t\) to \(o\)-FE is further favoured when lattice constants are fixed. This indicates that supersaturated Y doping can facilitate the formation of the \(o\)-FE phase.

**Outlook**

\(Pbc2\), ferroelectric phase is stabilized in HfO\(_2\)-Y bulk single crystals, with switchable polarization \(2P_c = 6\mu\)C cm\(^{-2}\) and coercive field \(E_c = 4\) MV cm\(^{-1}\). Abundant 90°/180° ferroelectric domain nature is unveiled in atomic imaging. Our findings break the upper length-scale limit for ferroelectric HfO\(_2\), provide insights for an alternative route for polymorphic phase controlling of HfO\(_2\), and pave the way for the further exploitation of hafnia-based science and technologies. The large sample size ensures several measurement techniques (such as neutron diffraction) feasible, and is sufficient for the use as substrate material. Moreover, the \(Pbc2\) phase crystal at room temperature and ambient pressure provides a great opportunity to study the possible antiferroelectricity and field-induced transitions in future. A recent work suggests that the \(Pbc2\) phase plays an important role as the intermediate phase of polarization switching\(^{33}\). A deeper investigation on the \(Pbc2\) phase in future could be the key to unravel the robust low-dimensional ferroelectricity mystery in HfO\(_2\).
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Methods

Sample growth. The HfO$_2$:Y single crystals were grown using a LDFZ technique. Stoichiometric and high-purity powders of HfO$_2$ and Y$_2$O$_3$ (900 °C baked overnight) were mixed in a mortar, pelletized and sintered at 1,500 °C in a box furnace for 20 h with one intermediate grinding. The sintered pellet was grinded into powder, poured into a rubber tube, and pressed into a 3-mm-diameter rod under 8,000 psi hydrostatic pressure. The compressed rod was sintered at 1,600 °C in a box furnace for 10 h. The crystals were grown at the speed of 20 mm h$^{-1}$ in 0.5 l/min O$_2$. This growth speed is fast enough to prevent phase separation and slow enough to guarantee good crystallinity. Laser power of 95% is needed to melt the refractory HfO$_2$.

Neutron diffraction. For the NPD measurements, an approximately 2-g single crystal was finely ground and loaded in a vanadium can of 3 mm in diameter. NPD measurements were performed on the time-of-flight powder diffractometer, POWGEN, located at the Spallation Neutron Source at Oak Ridge National Laboratory. The data were collected with neutrons of central wavelength of 0.8 Å.

TEM measurements. Specimens for (S)TEM studies were fabricated in four cutting single crystals including [111], [010], [100] and [001] axes by mechanical polishing, followed by Ar-ion milling and studied using JEOL-2000FX TEM and JEOL-2010F TEM. Due to the high-density polishing, followed by Ar-ion milling and studied using JEOL-2010F TEM and 512 imaging was conducted using a spherical aberration-corrected transmission electron microscope (JEOL-2100F) and acquired in two conditions: 512 × 512 at 500 kV and 1,600 V. The plane-wave cutoff energy is 50 Ry. The atomic force convergence threshold is set as 5 × 5 × 5 nm$^3$. An in situ heating TEM experiment was carried out using a JEOL-2000FX TEM with a high-temperature specimen holder. All images show raw data.

DFT calculations. Density-functional theory (DFT) calculations are carried out with the ABINIT package for structure optimizations of bulk HfO$_2$ with fixed lattice modes and the Quantum-espresso package for structural relaxations of Y-doped HfO$_2$. The exchange-correlation functional is approximated with the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional, as implemented in the Quantum-espresso (QE) code. The plane-wave cutoff energy is 50 Ry. The atomic force convergence threshold is set as 5 × 5 × 5 nm$^3$. An in situ heating TEM experiment was carried out using a JEOL-2000FX TEM with a high-temperature specimen holder. All images show raw data.