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Epitaxial Stabilization versus Interdiffusion: Synthetic Routes to Metastable Cubic HfO$_2$ and HfV$_2$O$_7$ from the Core—Shell Arrangement of Precursors

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Metastable materials that represent excursions from thermodynamic minima are characterized by distinctive structural motifs and electronic structure, which frequently underpins new function. The binary oxides of hafnium present a rich diversity of crystal structures and are of considerable technological importance given their high dielectric constants, refractory characteristics, radiation hardness, and anion conductivity; however, high-symmetry tetragonal and cubic polymorphs of HfO$_2$ are accessible only at substantially elevated temperatures (1720 and 2600°C, respectively). Here, we demonstrate that the core—shell arrangement of VO$_2$ and amorphous HfO$_2$ promotes outward oxygen diffusion along an electropositivity gradient and yields an epitaxially matched V$_2$O$_7$/HfO$_2$ interface that allows for the unprecedented stabilization of the metastable cubic polymorph of HfO$_2$ under ambient conditions. Free-standing cubic HfO$_2$, otherwise accessible only above 2600°C, is stabilized by acid etching of the vanadium oxide core. In contrast, interdiffusion under oxidative conditions yields the negative thermal expansion material HfV$_2$O$_7$. Variable temperature powder X-ray diffraction demonstrate that the prepared HfV$_2$O$_7$ exhibits pronounced negative thermal expansion in the temperature range between 150 and 700°C. The results demonstrate the potential of using epitaxial crystallographic relationships to facilitate preferential nucleation of otherwise inaccessible metastable compounds.

Introduction

Metastable crystal structures with atomic connectivities somewhat altered from the thermodynamic phase correspond to relatively shallower local minima on free energy landscapes but can in many instances be trapped under ambient conditions. The large amounts of energy inputted in conventional high-temperature ceramic and metallurgical processing methods result in reaction mixtures being able to efficiently approach equilibrium. In contrast, synthetic approaches that can situate the material in a local minimum under specific constraints (temperature, pressure, voltage, strain, chemical doping) can often be rapidly “quenched”, enabling kinetic trapping of metastable atomic configurations. Perhaps the most iconic example of a metastable material that can be isolated under ambient conditions is diamond, which exhibits a distinctly shallower local minima on free energy landscapes but can in many instances be trapped under ambient conditions. In contrast, annealing core—shell VO$_2$ nanocrystals and amorphous HfO$_2$ nanocrystals under oxidative conditions promotes effective interdiffusion, stabilizing the negative thermal expansion material, HfV$_2$O$_7$. Perhaps the most iconic example of a metastable material that can be isolated under ambient conditions is diamond, which exhibits a distinctly shallower local minima on free energy landscapes but can in many instances be trapped under ambient conditions. In contrast, annealing core—shell VO$_2$ nanocrystals and amorphous HfO$_2$ nanocrystals under oxidative conditions promotes effective interdiffusion, stabilizing the negative thermal expansion material, HfV$_2$O$_7$. HfO$_2$ and ZrO$_2$ are commonly referred to as the “twin oxides” owing to the similarities in the properties of these two materials that arises from the closely matched atomic radii of their cations, which indeed is a direct result of lanthanide contraction. Under ambient conditions, hafnia crystallizes in a low-symmetry (seven-coordinated hafnium atoms) monoclinic phase ($M$, space group $P2_1/c$) and...
exhibits a diffusionless Martensitic transition to a higher-symmetry (with eight-coordinated hafnium atoms) tetragonal structure (R, space group P4/2/mmc) at a temperature of ca. 1720°C. An even higher symmetry (still with eight-coordinated hafnium atoms) cubic phase (C, space group Fm3m) is stabilized at temperatures above 2600°C and is retained until hafnia is congruently melted at a temperature of 2758°C. Traversing the free energy landscape along the pressure axis reveals two oxygen-deficient orthorhombic variants, orthorhombic I (O1, space group Pca21), which is stabilized above 4.3 GPa and orthorhombic II (O2, space group Pmn21), which is observed above 14.5 GPa. The dielectric constant of monoclinic HfO2 is in the vicinity of 18, substantially higher than that of SiO2, whereas tetragonal and cubic polymorphs are predicted to have dielectric constants approaching 70 and 30, respectively.

By reacting HfCl4 with hafnium(IV) tert-butoxide (HF(OtBu)4) with the addition of low concentrations of the less reactive cerium(IV) tert-butoxide and lanthanum(III) isopropoxide, we have recently separated nucleation and growth steps, enabling the stabilization of HfO2 nanocrystals with dimensions <10 nm. The development of this synthetic route reveals the critical threshold for stabilizing tetragonal HfO2 as being 3.6–3.8 nm. Another approach to stabilization of tetragonal HfO2 involves the introduction of multiple nanowhiskers within the monoclinic variant; the twin planes serve to nucleate the transformation dislocation and mediate stabilization of the tetragonal phase at temperatures more than 1000°C lower than the bulk transformation temperature. While these efforts have enabled stabilization of the technologically important tetragonal polymorph of HfO2, the higher temperature cubic phase remains difficult to access. Allovalent doping has been utilized to stabilize cubic HfO2 but requires dopant concentrations as high as 11.0 and 3.00 at.%. In the first step, 30 mg of nanowires or quasi-spherical nanocrystals of VO2 crystallized in the M1 phase were dispersed in 80 mL dry ethanol (dried over molecular sieves with 4Å pore size and Na2SO4 via ultrasonication (Branson SS10) for ca. 10 min. The colloidal dispersion was then placed within a three-neck round-bottomed flask, which was attached to an Ar Schlenk line and cooled using an ice bath. Hf(OtBu)4 was added dropwise to the ethanol dispersion at a molar ratio of VO2:Hf(OtBu)4 of 1:0.5 under an Ar ambient; the reaction mixture was then allowed to stir for 20 min. This dispersion was then removed from the ice bath, placed on a heating mantle, and heated to 80°C while maintaining an Ar ambient. Next, 20 mL of a 1:20 (v/v) H2O:EOH mixture was added dropwise to initiate hydrolysis of the hafnium alkoxide. The low water content precludes homogeneous nucleation of HfO2 nanocrystals in solution and constrains HfO2 deposition to the surfaces of the VO2 nanocrystals. The reaction mixture was maintained at 80°C for 15 min and subsequently removed from heat and allowed to cool to ca. 50°C before moving to centrifugation. The solid precipitate was then recovered by centrifugation at 8700 rpm using a Heraeus Megafuge 8. The recovered solid was resuspended in ethanol and recovered by centrifugation at 8700 rpm. Two such cycles were performed. The annealed powders precipitated from the core—shell nanocrystals were placed in a 5.67 M HNO3 solution and remnant VO2 from the core. The acid-treated sample was sonicated vigorously for ca. 1 h to ensure dissolution of the core. The supernatant turned light blue in color and was analyzed upon cooling to room temperature before further analysis.

Quasi-spherical VO2 nanocrystals with a diameter of 44±30 nm have been prepared by an alternative sol–gel condensation and hydrothermal treatment route. Briefly, VO(OH)2 was precipitated from the reaction between NH4VO3 and NH4H2O in deionized water at a temperature of 80°C. The solid precipitate was then heated at 210°C for 24 h within the hydrothermal apparatus described above. The recovered powder was washed with copious amounts of water and acetone across three cycles of resuspension and centrifugation.

Deposition of HfO2 onto VO2 Nanocrystals: Amorphous HfO2 shells were deposited onto nanowires and quasi-spherical nanocrystals of VO2 through a hydrolysis approach analogous to the Stöber method for the preparation of SiO2 shells. In the first step, 30 mg of nanowires or quasi-spherical nanocrystals of VO2 crystallized in the M1 phase were dispersed in 80 mL dry ethanol (dried over molecular sieves with 4Å pore size and Na2SO4 via ultrasonication (Branson SS10) for ca. 10 min. The colloidal dispersion was then placed within a three-neck round-bottomed flask, which was attached to an Ar Schlenk line and cooled using an ice bath. Hf(OtBu)4 was added dropwise to the ethanol dispersion at a molar ratio of VO2:Hf(OtBu)4 of 1:0.5 under an Ar ambient; the reaction mixture was then allowed to stir for 20 min. This dispersion was then removed from the ice bath, placed on a heating mantle, and heated to 80°C while maintaining an Ar ambient. Next, 20 mL of a 1:20 (v/v) H2O:EOH mixture was added dropwise to initiate hydrolysis of the hafnium alkoxide. The low water content precludes homogeneous nucleation of HfO2 nanocrystals in solution and constrains HfO2 deposition to the surfaces of the VO2 nanocrystals. The reaction mixture was maintained at 80°C for 15 min and subsequently removed from heat and allowed to cool to ca. 50°C before moving to centrifugation. The solid precipitate was then recovered by centrifugation at 8700 rpm using a Heraeus Megafuge 8. The recovered solid was resuspended in ethanol and recovered by centrifugation at 8700 rpm. Two such cycles were performed. The annealed powders precipitated from the core—shell nanocrystals were placed in a 5.67 M aqueous solution of HCl at a concentration of 1 mg solid per mL of solution. The prepared dispersion had a pH <1, which results in the dissolution of VO2 and remnant VO2 from the core. The acid-treated sample was sonicated vigorously for ca. 1 h to ensure dissolution of the core. The supernatant turned light blue in color indicating the stabilization of vanadium oxide clusters. The solid was then recovered by centrifugation at 8700 rpm. The recovered solid was subsequently resuspended in ethanol and collected by centrifugation at 8700 rpm two times before being allowed to dry at room temperature.

Stabilization of Cubic HfO2 by Dissolution of the VO2 Core of V2O5@HfO2 Core—Shell Nanocrystals: After annealing to obtain V2O5@HfO2 core—shell nanocrystals, the vanadium oxide shell was etched in acid solution to stabilize cubic HfO2. Specifically, V2O5@HfO2 core—shell nanocrystals were placed in a 5.67 M aqueous solution of HCl at a concentration of 1 mg solid per mL of solution. The prepared dispersion had a pH <1, which results in the dissolution of V2O5 and remnant VO2 from the core. The acid-treated sample was sonicated vigorously for ca. 1 h to ensure dissolution of the core. The supernatant turned light blue in color indicating the stabilization of vanadium oxide clusters. The solid was then recovered by centrifugation at 8700 rpm. The recovered solid was subsequently resuspended in ethanol and collected by centrifugation at 8700 rpm two times before being allowed to dry at room temperature.

Synthesis of HfV2O7: V2O5@HfO2 core—shell nanocrystals were prepared as discussed above and the recovered powders were placed in a quartz tube and annealed under a static air ambient within a tube furnace ramping at a rate of 20°C/min to 650°C. The furnace was maintained at 650°C for 25 min. The recovered solid was light orange in appearance and was analyzed upon cooling to room temperature.

Characterization: Low-magnification transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2010
results in the dissolution of the V₂O₃ core and after F) washing with ethanol yields phase-pure cubic HfO₂, which is recovered upon centrifugation.

In-situ powder X-ray diffraction (XRD) experiments were performed using a Bruker D8-Vario X-ray powder diffractometer using Cu Ka (λ=1.5418Å) source operated at a 40 kV accelerating voltage with a 40 mA current. An MTC oven attachment was used for the heating of powder XRD patterns were performed for patterns recorded using a Bruker D8 Advance Eco X-Ray powder diffractometer (λ=1.5418Å) environment, with patterns recorded at 50°C intervals. Refinements of powder XRD patterns were performed for patterns recorded using a Bruker D8 Advance Eco X-Ray powder diffractometer with a Cu Ka (λ=1.5418Å) source scanning at 1.9°/min.

Fourier transform infrared (FTIR) data was acquired using a Bruker VERTEX-70 FTIR instrument equipped with a PIKE MIIRace single-reflection horizontal attenuated total reflectance (ATR) accessory. Neutron Activation Analysis (NAA) was performed using the Texas Engineering and Experiment Station 1-MW TRIGA reactor. Neutron irradiations of 30 s were performed at a thermal neutron fluence rate of 9.1×10¹² cm⁻².s⁻¹. γ-ray spectra were obtained using an HPGe detector for 500 s after a 270 s decay interval. Data analyses were performed using software from Canberra Industries.

Results and Discussion

Stabilizing Metastable Cubic HfO₂:

VO₂ nanowires with lateral dimensions of 180±70 nm and lengths of 1.6±0.9 μm have been prepared by the acetone reduction of V₂O₅ under hydrothermal conditions as discussed in detail in the Methods section.36–38 Quasi-spherical VO₂ nanocrystals with diameters of 44±30 nm have been prepared by sol—gel reduction—condensation of NH₄VO₃ with hydrazine followed by hydrothermal treatment, also as discussed in the Methods section.36–39,40 Figures S1A and B (Supporting Information) show representative transmission electron microscopy (TEM) images of the as-prepared VO₂ nanowires and quasi-spherical nanocrystals, respectively. Figure S1C plots their corresponding powder X-ray diffraction (XRD) patterns, attesting to the crystallization of both the nanowires and the nanocrystals in the monoclinic M1 phase. Pronounced Scherrer broadening is observed in the XRD pattern acquired for ultrasmall VO₂ nanocrystals owing their small X-ray coherent domain sizes.

The synthetic approach to core—shell positioning of the precursors and the process used to prepare metastable cubic HfO₂ and the negative thermal expansion material, HfV₂O₇, is illustrated in Figure 1. An amorphous HfO₂ shell is first deposited onto VO₂ nanowires or VO₂ nanowires by hydrolysis and condensation of a hafnium alkoxide precursor as per:

\[ \text{Hf(OBu}_3\text{)}_4 + 2 \text{H}_2\text{O} + 2 \text{H}_2\text{O} \rightarrow \text{HfO}_2 \text{O}_7 + 4 \text{ROH} (aq.) \] (1)

This reaction is performed at low temperature (4°C) to prevent homogeneous nucleation of HfO₂ nanocrystals. The abundant hydroxyl groups on the surfaces of the VO₂ nanocrystals allow for formation of V-O-Hf oxo linkages as observed previously in the deposition of SiO₂ shells.36,37

Powder XRD patterns acquired along the synthetic scheme sketched in Figure 1 are shown in Figure S2 providing evidence for the phase
Figure 2: TEM and SEM images corresponding to synthetic steps involved in the stabilization of cubic HfO$_2$. A) TEM image (top) and SEM image (bottom) of M1-phase VO$_2$ nanowires prepared by the hydrothermal reduction of V$_2$O$_5$ by acetone. B) TEM and SEM images of VO$_2$ nanowires coated with an amorphous HfO$_2$ shell. C) TEM and SEM images of V$_2$O$_5$@cubic-HfO$_2$ core—shell structures obtained upon annealing VO$_2$@amorphous-HfO$_2$ structures at 650°C. D) TEM and SEM image of polycrystalline cubic HfO$_2$ after acid etching of the V$_2$O$_5$ core.

Additional evidence for the core-shell configuration comes from examination of micromotened nanowires. Figures 3A and B show low-magnification TEM images of core—shell V$_2$O$_5$@HfO$_2$ nanowires obtained upon annealing alongside an energy-dispersive X-ray spectroscopy (EDX) map illustrating the core—shell arrangement of the vanadium and hafnium oxide domains. Figure 3A shows a cross-sectional image, whereas Figure 3B exhibits a cross-sectional image and EDX map acquired for an ultramicrotomed nanowire. This image shows that vanadium (red) is concentrated within the core of the structure, whereas hafnium (green) is concentrated within the shell. Further evidence of the core—shell structure comes from Figure 5S, which shows a cross-sectional view of an ultramicrotomed nanowire as well as an EDX line scan that further confirms the core—shell structure with Hf concentrated within the shell and vanadium within the core. Some V content is detected within the shell likely derived from the outwards diffusion of vanadium cations facilitated by the miscibility of the two cations. The lattice-resolved HRTEM images in Figures 3C and D demonstrate the epitaxial matching between the rhombohedral V$_2$O$_5$ core and cubic HfO$_2$ shell. The direction of epitaxy in the interfacing phase is further indicated in Figure S6 a-d. Figures S6 e and f show the parallel green-dashed arrows along (-111) diffraction spots of cubic HfO$_2$ and (-1-10) diffraction spots of rhombohedral V$_2$O$_5$, which confirms the epitaxy between two phases. Figures 3D and E delineate lattice spacings of 2.95 ± 0.08 Å corresponding to the separation between (111) planes of cubic-HfO$_2$ and 2.68 ± 0.07 Å corresponding to the separation between (1-20) planes of rhombohedral V$_2$O$_5$. Indeed, this epitaxial matching is critical to the nucleation of cubic HfO$_2$.

The dynamical evolution of VO$_2$ nanoparticles coated with amorphous HfO$_2$ shells upon thermal annealing has been examined by in situ powder X-ray diffraction and transmission electron microscopy. Figure 4A plots intensity modulation maps illustrating the evolution of the powder XRD patterns of VO$_2$@amorphous HfO$_2$ core—shell structures as a function of temperature upon annealing under a N$_2$ ambient. Reflections corresponding to the M1 phase of VO$_2$ disappear at ca. 590—600°C and reflections that can be indexed to cubic HfO$_2$ emerge in the temperature range of 560—675°C. The crystallization and reduction of VO$_2$ to V$_2$O$_5$ occurs in concert and involves oxygen diffusion along a gradient of electropositivity. As noted above, oxygen vacancies are strongly destabilized as a result of the electropositive nature of hafnium.
of crystallization and thus oxygen atoms diffuse from the vanadium oxide core to incipient crystalline HfO₂ domains resulting in a decrease in the formal valence of vanadium within the core. Fig. 4B shows the results of an identical reaction performed without the presence of VO₂. Initially nucleated cubic/tetragonal domains are lost and the thermodynamically stable monoclinic phase of HfO₂ is stabilized as a result of grain growth. The epitaxial relationship between V₂O₃ and cubic HfO₂ in the crystalline core—shell structures is therefore critical to preventing reversion to the thermodynamically stable monoclinic polymorph at elevated temperatures. Fig. 5 shows high-resolution TEM images along with corresponding selected area electron diffraction patterns acquired upon in situ annealing of core—shell configurations of VO₂ nanocrystals with an amorphous HfO₂ shell. The initially amorphous HfO₂ domains are transformed to cubic HfO₂ at ca. 560°C and such domains persist upon heating up to 700°C. Cubic HfO₂ and rhombohedral V₂O₃ domains are clearly discernible upon annealing to 560°C. Fig. 5 shows the crystallite size of cubic-HfO₂ is 8.4±1.4 nm.

HfO₂ exhibits high stability in aqueous media across a wide pH range; in contrast, V₂O₃ is readily dissolved in acidic media. This difference in reactivity provides a means of isolating free-standing cubic HfO₂ powders. The V₂O₃ cores of V₂O₃@HfO₂ core—shell structures have been etched in acid solution at room temperature, thereby preserving the metastable cubic structure of the shell. Refinement of the powder XRD pattern provides corroboration of the cubic crystal structure, which crystallizes in the Fm3m space group with a lattice constant of 𝑎 = 5.04793(22)Å (Fig. 4D and Table S1). Fig. 4C shows a lattice-resolved image of free-standing cubic HfO₂ particles (prepared by acid etching of core-shell V₂O₃@HfO₂) acquired along the [110] zone axis. Based on analysis of the powder XRD pattern and lattice-resolved TEM images, the recovered materials are phase pure. Fig. S7 shows an O-H stretching peak at 3315 cm⁻¹ in a FTIR spectrum acquired for the acid-etched sample indicating the presence of Hf(OH)₃ species after aqueous acid treatment.

Neutron activation analysis (NAA) quantification of the recovered solids reveals a V concentration of ca. 7.18±0.17 at.%, likely derived from the diffusion of vanadium atoms from within the core given the reasonable solubility of vanadium within the hafnia lattice. Notably, vanadium incorporation alone cannot account for stabilization of the metastable cubic polymorph; previous studies have indicated the need for at least 11 at.% V dopant incorporation to stabilize cubic HfO₂, which is observed to further be contaminated by HfV₃O₁₀. The stabilization of cubic HfO₂ stems from both kinetic origins as well as from the conditions of constrained equilibrium imposed by the small crystallite size. The change in free energy accompanying a transition from a thermodynamically stable (TS) to metastable (MS) phase can be described by the following expression:

\[ \Delta G_{\text{TS}→\text{MS}} = G_{\text{TS}} - G_{\text{MS}} + U_{\text{TS}} - U_{\text{MS}} + S_{\text{TS}} - S_{\text{MS}} \]  

where \( G_\text{TS} \) and \( G_\text{MS} \) denote the chemical free energy (dependent on temperature owing to entropic contributions), strain energy, and surface energy, respectively; the subscripts TS and MS denote the thermodynamic and metastable polymorphs, respectively. In order for cubic HfO₂ to emerge as the thermodynamically stable phase, the strain and surface energy terms have to strongly favor stabilization of the cubic polymorph. Recent calculations suggest that surface facets of cubic HfO₂ can indeed be substantially lower in energy.

Surface energy scales with particle diameter (D) as:

\[ \Delta G \propto (\frac{\gamma_s}{D}) \]  

where \( \gamma_s \) terms represent the surface energies of thermodynamic and metastable configurations, respectively; \( g = A_s/\gamma_s \) is the ratio of the interfacial surface areas for the two polymorphs. As such, nanoscale dimensions favor stabilization of the cubic polymorph.

Recent work has illustrated that a metastable polymorph can be preferentially stabilized if the barrier to nucleation of a metastable polymorph is lower than that of the thermodynamic phase. The barrier to nucleation can be written as:

\[ \Delta G_n \propto (\frac{\gamma_s}{-RT\ln a}) \]  

where \( \gamma_s \) is the interfacial surface energy of the nucleus, \( a \) is the ratio of interfacial surface areas for the two polymorphs, respectively.
where \( \eta \chi \) is the surface energy (equivalent to \( S \)), \( \sigma \) represents the supersaturation, and thus \(-RT\ln\sigma\) is the thermodynamic driving force for crystallization.\(^{53,54}\) If the surface energy of the metastable phase is lower, it can still be preferentially crystallized despite having a lower thermodynamic driving force for crystallization. The rhombohedral \( \text{V}_2\text{O}_3 \) core essentially selects for the preferential formation of cubic \( \text{HfO}_2 \) as compared to other \( \text{HfO}_2 \) polymorphs owing to the available epitaxial relationship (as well as the influence of vanadium incorporation). In other words, the coherent low-energy interface accessible between cubic-\( \text{HfO}_2 \) and rhombohedral \( \text{V}_2\text{O}_3 \) (but not with monoclinic \( \text{HfO}_2 \)) facilitates selective crystallization of the former polymorph by depressing the nucleation barrier. Interestingly, while the epitaxial relationship likely underpins nucleation of cubic \( \text{HfO}_2 \), the lattice mismatch is sufficiently large such as to bring about strain-induced delamination of the \( \text{V}_2\text{O}_3 \) core from the \( \text{HfO}_2 \) shell and this mismatch is further evidenced in the small crystallite size of the stabilized domains (Figs. 3B and S5). Indeed, the crystallite size of cubic-\( \text{HfO}_2 \) is 8.4±1.4 nm, which suggests that extended coherent interfaces are not stabilized within this system.

Figure 4: Temperature-dependent XRD patterns and structure refinement. A) Evolution of XRD patterns of \( \text{VO}_2@\text{amorphous HfO}_2 \) with increasing temperature. The (011) reflection of M1 \( \text{VO}_2 \) is attenuated as the (111) reflection for cubic hafnia begins to reach maximum intensity between 560 and 600°C. Crystal structures of the phases that are predominant within each temperature range are illustrated alongside the intensity map. B) Evolution of the powder XRD pattern in a control experiment omitting the \( \text{VO}_2 \) nanowires. Initially stabilized tetragonal/cubic \( \text{HfO}_2 \) domains disappear rapidly with sintering; the thermodynamically stable monoclinic phase of \( \text{HfO}_2 \) emerges as the dominant species. C) HRSTEM image of cubic \( \text{HfO}_2 \) along the [110] zone axis. The superimposed olive spheres are Hf atomic column positions in the [110] zone as predicted using CrystalMaker software. D) Observed XRD pattern (black crosses) plotted along with a refinement to cubic \( \text{HfO}_2 \). The simulated XRD pattern is displayed in red, background in green, and residual curve in blue; 20 positions of reflections are marked as purple ticks. The structure refines to cubic \( \text{HfO}_2 \) crystallized in the Fm\( 3m \) space group (see Table S1 for refinement metrics).
The stabilization of free-standing cubic hafnia thereby provides access to a metastable kinetically trapped polymorph that is otherwise only accessible at temperatures above 2600°C. The cubic HfO₂ remains stable for over 12 months without transforming to metastable tetragonal or thermodynamically stable monoclinic polymorphs.

**Synthesis of Negative Thermal Expansion HfV₂O₇**: Conventional routes to the synthesis of HfV₂O₇ employ the grinding and sintering at 700°C of hafnyl oxalic acid and ammonium oxodioxalato-vanadium nH₂O complexes in precise stoichiometric amounts. Other methods require copious amounts of organic solvents. Here we demonstrate that annealing VO₂@amorphous-HfO₂ core—shell nanowires under static air instead of Ar yields HfV₂O₇ by dint of an interdiffusion reaction (albeit without preservation of the nanowire morphology) as per:

\[ 4\text{VO}_2(s) + 2\text{HfO}_2(s) + \text{O}_2(g) \rightarrow 2\text{HfV}_2\text{O}_7(s) \]  

(2)

The reaction is strongly enthalpically favored and entropically disfavored. As such, a lower reaction temperature is imperative to facilitate high reaction yields but requires mitigating kinetic impediments to mixing of the precursors. The core-shell positioning of precursors outlined here allows for facile interdiffusion at relatively low temperatures enabling high conversion yields. **Figure 6** shows SEM and TEM images and an XRD pattern indicating the synthesis of HfV₂O₇. The core-shell structuring of precursors thus enables a facile low-temperature route for the stabilization of HfV₂O₇, which is an isotropic negative thermal expansion material.

**In situ** XRD data has been acquired to examine the evolution of products with increasing temperature. **Figure 7** shows variable-temperature powder X-ray diffraction data acquired for the HfV₂O₇ materials obtained by this approach. The evolution of two prominent reflections, (440) and (422), is shown in **Figure 7**. For both sets of reflections, a shift of 2θ to lower values is initially observed (until a temperature of 150°C), followed by a subsequent increase to higher 2θ values up to 700°C. The initial increase and subsequent decrease of interplanar lattice separation with increasing temperature is indicative of the straightening of VO₂—O—VO₂ bonds and the subsequent transverse, volume-reducing oscillations of said bonds. The negative thermal expansion behavior is observed to be entirely reversible in the cooling panels of **Figure 7**.

**Conclusions**

In summary, we have demonstrated a facile low-temperature synthetic route for stabilizing the metastable cubic phase of HfO₂ under ambient conditions utilizing the epitaxial relationship between rhombohedral V₂O₃ (generated *in situ* from reduction of VO₂ as a result of oxygen diffusion) and cubic HfO₂. Oxygen diffusion proceeds from the VO₂ core to the amorphous HfO₂ shell owing the more electropositive nature of the latter and the higher oxygen vacancy formation energy in crystalline HfO₂ as compared to amorphous HfO₂; the available epitaxial relationship along with incorporation of vanadium atoms reduces the barrier to nucleation of the cubic polymorph notwithstanding its metastable nature and allows for its preservation at elevated temperatures wherein sintering and grain growth strongly favors stabilization of the monoclinic phase. The formation of a low-energy coherent interface substantially reduces the barrier to nucleation of cubic HfO₂ domains despite its relatively lower thermodynamic driving force for crystallization as compared to the monoclinic phase. The epitaxial synthesis route thus serves as a valuable addition to strategies such as size reduction and introduction of twin domains used to stabilize metastable polymorphs of HfO₂.

The arrangement of VO₂ and HfO₂ in a core—shell structure further provides a direct solid-state synthetic route to cubic HfV₂O₇, a technologically important negative thermal expansion material. The core-shell positioning of precursors allows for...
this entropically disfavored reaction to be performed at low temperatures with excellent conversion. Variable-temperature powder XRD measurements show pronounced negative thermal expansion behavior in the range between 150 and 700°C. Future work will focus on experimentally determining the dielectric constant of this polymorph as well as exploring epitaxial relationships with the rich available repertoire of VO₂ polymorphs to stabilize other metastable variants of HFO₂.

Conflicts of interest
There are no conflicts to declare.

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