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***In Situ* Determination of the HfO₂-Ta₂O₅-Temperature Phase Diagram up to 3000 °C**

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Abstract

The previously unknown experimental HfO₂-Ta₂O₅-temperature phase diagram has been elucidated up to 3000 °C using a quadrupole lamp furnace and conical nozzle levitator system equipped with a CO₂ laser, in conjunction with synchrotron X-ray diffraction. These in-situ techniques allowed the determination of: (i) liquidus, solidus and invariant transformation temperatures as a function of composition from thermal arrest experiments, (ii) determination of equilibrium phases through testing of reversibility via in-situ X-ray diffraction, and (iii) molar volume measurements as a function of temperature for equilibrium phases. From these, an experimental HfO₂-Ta₂O₅-temperature phase diagram has been constructed which is consistent with the Gibbs Phase Rule.

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I. Introduction

1.1 The $\text{HfO}_2\text{-Ta}_2\text{O}_5$ -Temperature system

The equilibria of the $\text{HfO}_2\text{-Ta}_2\text{O}_5$ system are of interest for applications in high temperature material systems¹. Compositions within this system are currently used as thermal barrier coatings²⁻⁵, and high temperature dielectrics⁶. Understanding of the $\text{HfO}_2\text{-Ta}_2\text{O}_5$ system is also of interest for the oxidation of other high temperature systems such as Hf-Ta ^{7,8}, Hf-Ta-C ⁹⁻¹³ and Hf-Ta-N ¹⁴ alloys.

The $\text{HfO}_2\text{-Ta}_2\text{O}_5$ system has three distinct compounds HfO_2 , $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ and Ta_2O_5 . HfO_2 has three polymorphs as a function of temperature^{15,16}: monoclinic, with $\text{P2}_1/\text{c}$ symmetry (space group (SG) 14) when $T < 1750^\circ\text{C}$, tetragonal¹⁷, with $\text{P4}_2/\text{nmc}$ symmetry (SG 137) when $1750^\circ\text{C} < T < 2600^\circ\text{C}$, cubic¹⁵, with $\text{Fm}\bar{3}\text{m}$ symmetry (SG 225) when $2600^\circ\text{C} < T < 2750^\circ\text{C}$ ¹⁸ and liquid at $T > 2750^\circ\text{C}$ ¹⁸. The molten structure of pure HfO_2 has been examined by Gallington *et al.*¹⁹ while the molten structure of Ta_2O_5 has been examined by Alderman *et al.*²⁰

$\text{Hf}_6\text{Ta}_2\text{O}_{17}$ was first identified by Spiridonov *et al.*²¹ and then soon after determined to be part of a homologous series by Turcotte *et al.*²² A homologous series is defined as a group of structures in which the difference between successive members is a simple structural unit, which also results in a closely spaced compositional variation. Yang *et al.*²³ showed that $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ superstructures could also be synthesised via oxidation. McCormack and Kriven²⁴ were able to solve the $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ superstructure (8-subcells stacked in the a-direction) with space group $\text{Ima}2$ (SG 46) and determined the homologous series regime to be $0.8 < \text{HfO}_2 < 0.888$. McCormack *et al.*^{24,25} then measured the thermal expansion as well as identified and characterized the peritectic transformation $\text{HfO}_2 + \text{Liq} \rightleftharpoons \text{Hf}_6\text{Ta}_2\text{O}_{17}$ at 2250°C .

Ta_2O_5 has two equilibrium polymorphs and two possible metastable polymorphs. The low temperature orthorhombic polymorph with $\text{Pmm}2$ ²⁶ (SG 25) symmetry ($\text{O-Ta}_2\text{O}_5$) undergoes a slow, reconstructive, reversible transition into the high temperature tetragonal polymorph having $\text{I4}_1/\text{amd}$ (SG 141)²⁷ symmetry ($\text{T-Ta}_2\text{O}_5$) at approximately 1360°C ²⁸. It is worth mentioning that Stephenson and Roth²⁹ presented a monoclinic, space group $\text{I}2$ (SG 5) alternative structure that is related to the tetragonal structure. They believed that this structure was more correct, but it has not been widely accepted in the community. Sufficiently slow cooling and/or annealing below the transition temperature (1360°C) transforms the $\text{T-Ta}_2\text{O}_5$ back into $\text{O-Ta}_2\text{O}_5$. However, even with fast cooling rates $>50^\circ\text{C/s}$, the $\text{T-Ta}_2\text{O}_5$ cannot be retained at room temperature. On cooling from $\text{T-Ta}_2\text{O}_5$, two metastable polymorphs forms. The first metastable polymorph forms at around 940°C with a proposed monoclinic symmetry of $\text{I}2$ ²⁷ (SG 5) ($\text{M}'\text{-Ta}_2\text{O}_5$). The second metastable polymorph forms around 320°C as orthorhombic with a proposed symmetry of Imma (SG 74) ($\text{O}'\text{-Ta}_2\text{O}_5$)²⁷. These polymorphs are considered to be metastable as they can only be formed on cooling. They do not show reversibility. Turcotte *et al.*²² suggested that Ta_2O_5 formed a homologous series with the addition of HfO_2 . No information regarding the change in structure or range was provided.

Turcotte *et al.*²² collected preliminary liquidus data from thermal arrest experiments but did not mention any invariant transformations. The next step for developing the $\text{HfO}_2\text{-Ta}_2\text{O}_5$ -temperature phase space is to: (i) identify the equilibrium phases and (ii) to start collecting thermophysical data for CALPHAD modelling. These are the two main goals of the present study.

1.2 Building accurate phase diagrams

Most applications of ceramics rely on a fundamental knowledge of phase diagrams generated from phase equilibria, the accompanying phase transformations, as well as microstructure-property relations. These features are integral in the design of all classes of ceramic materials. There are three main stages in the development of accurate phase diagrams: (i) Equilibrium phase identification as function of thermodynamic variables (T, P, n_i), (ii) measurement of thermodynamic parameters ($\frac{\partial G}{\partial T} = S, \frac{\partial(G/T)}{\partial T} T^2 = H, \frac{\partial G}{\partial P} = V, \frac{\partial G}{\partial n_i} = \mu_i$) and (iii) modelling of free energy, G from the thermodynamic parameters using the CALPHAD (CALculation of PHase Diagrams) method³⁰.

The CALPHAD method involves modelling the free energies, $G_j(T, P, n_i)$ of a series of phases, j within a system, using the measured or calculated thermodynamic parameters (S, H, V, μ_i). The equilibrium phases will be those with the lowest free energy under the specified conditions (T, P and n_i). While this method is extremely powerful for building accurate phase diagrams, it can only be applied in cases where the correct equilibrium phases have been identified and characterized. If an equilibrium phase has been missed and is not included in the CALPHAD calculation, CALPHAD will not be able to predict its existence. This highlights the importance of the first step of experimental equilibrium phase identification.

Experimentally, two key features can be used to identify an equilibrium phase: (i) Thermodynamic parameters are constant when thermodynamic variables are constant i.e. the system is not changing under constant T, P and n_i . (ii) Equilibrium phase reversibility ($A \rightleftharpoons B$) i.e. when a phase transformation occurs at its equilibrium conditions, reaction will occur in the forward and reverse direction for any perturbation in thermodynamic variables. Conversely, a non-equilibrium phase is one which does not follow either of these key features. It can be difficult to distinguish equilibrium phases from non-equilibrium phases, as non-equilibrium phases can become kinetically stabilized. With respect to the free energy, these kinetically stabilized phases are trapped in a local minimum, which require additional kinetic energy to achieve the equilibrium phase, i.e. move to the global minimum. As such, these kinetically stabilised phases will not exhibit phase reversibility for any perturbation in thermodynamic variable.

These factors have led to mis-identification of equilibrium phases from *ex situ* experiments which involve heating samples to a temperature of interest where they are held isothermally, then quenched (cooled rapidly to ambient conditions). The large cooling rate from quenching is assumed to kinetically entrap the equilibrium phase from the isothermal hold. However, in some systems, this processing can induce the formation of non-equilibrium phases or even miss high temperature equilibrium phases due to fast transformations on cooling.

Due to these factors, *in situ* at temperature experiments will be used to elucidate high temperature (3000 °C) $\text{HfO}_2\text{-Ta}_2\text{O}_5$ -Temperature phase space accurately and efficiently. The two key experiments performed are: (i) Thermal arrest measurements³¹ using a conical nozzle levitator (CNL) system equipped with a 400 W CO_2 laser³² and (ii) *in situ* X-ray powder diffraction (XRPD) in conjunction with the quadrupole lamp furnace^{17,33-37} (QLF) and CNL equipped with 400 W CO_2 laser systems³². The thermal arrest experiments will determine the liquidus, solidus and invariant transformation temperatures while the *in situ* XRPD will allow for equilibrium phase identification,

verification of transformation reversibility and measurements of the molar volume (thermodynamic parameter $\frac{\partial G}{\partial P} = V$) as a function of temperature and composition by Rietveld refinement³⁸. These *in situ* volume measurements can be used for future CALPHAD calculations to further refine the HfO₂-Ta₂O₅ phase diagram.

II. Experimental Procedures

2.1 Powder synthesis and preliminary characterization

Hafnium tantalate powders were synthesized by the organic steric entrapment of cations^{39–41}. Hafnium (IV) chloride, 99.9 % (metal basis) (Alfa Aesar, Inc., Ward Hill, MA, USA) was dissolved in deionized water. Tantalum (V) chloride, 99.99 % (metal basis) (Alfa Aesar, Inc., Ward Hill, MA, USA) was dissolved in isopropanol. The masses of hafnium (IV) chloride and tantalum (V) chloride were determined based on cation stoichiometry of the oxide being fabricated. The two solutions were mixed and stirred for one hour. Ethylene glycol (Aldrich Chemical Company, Milwaukee, WI, USA) having a molecular weight of 67.07 amu, was added in the proportion to maintain a cation valence charge to monomer charge ratio of four. After the addition of the steric entrapment agent (ethylene glycol), the solution was stirred for 1 h at room temperature, followed by heating at 300 °C, until enough water and isopropanol were evaporated, forming a viscous gel. The gel was subsequently dried overnight at 100 °C to produce a dry, porous mass.

The porous mass was then ground in a zirconia mortar and pestle, calcined and crystallized, at 1050 °C for 3 h in a zirconia crucible, at a heating and cooling rate of 10 °C/min. The powders were then pressed into pellets in a Carver press (standard bench top press 3850, Carver, Inc., Wabash, IN, USA) at a load of ~60 MPa. These pellets were then annealed at 1300 °C in a platinum crucible for 10 h at a heating and cooling rate of 10 °C/min. The annealed powders were then ground and sieved to <45 µm.

Crystalline phase composition of the samples was examined by powder X-ray diffraction (XRD) with a Bruker D5000 diffractometer (Bruker AXS Inc., Madison, WI, USA), using CuK_α radiation ($\lambda = 1.5418$ Å, 40 kV, 30 mA). XRD patterns were acquired over a 2 θ range of 10 ° to 65 ° at 1 °/min and step size of 0.02 °. The crystalline phase was identified with reference to the International Centre for Diffraction Data PDF-4+ database (ICDD v. 2015, International Centre for Diffraction Data, Newton Square, PA) accessed through Jade 9.4.1 software (Materials Data Inc., Livermore, CA, USA).

Elemental composition was measured by X-ray fluorescence (XRF) spectroscopy in a Shimadzu EDX-7000 (Shimadzu America Inc., Chicago, IL, USA) by collecting characteristic X-rays for elemental hafnium and tantalum. The room temperature composition measured from XRF and phase fractions for each sample synthesized are summarized in Table 1.

2.2. Thermal arrest from cooling traces

The hafnium tantalate ($\text{HfO}_2 \bullet \text{Ta}_2\text{O}_5$) powders were melted into polycrystalline spheroids 2-3 mm in diameter in a copper hearth, in air, with a 400 W sealed CO_2 laser (where a 10.6 μm beam had a 5 mm diameter at a 1 m away from the laser, Synrad FSi401SB, Mukilteo, WA, USA). The laser power of the beam was adjusted by a LabVIEW (National Instruments, Austin, TX, USA) controlled laser controller (Synrad UC-2000) which allowed incrementation of the power by 0.5 %. The surface tension of the oxide melt tended to form spheroidal beads.

Cooling profiles on recalescence³¹ of the hafnium tantalate beads in air were recorded and analyzed. Selected beads were levitated and rotated in a conical nozzle levitator³² (CNL) in air, while being heated with a laser. This method has been described in more detail by McMurray et al³¹ and Ushakov. Temperatures on laser melting and cooling traces during quenching from the liquid state were simultaneously monitored using two pyrometers. In addition to a fast, single-band pyrometer (900 nm, 10 ms response time, 700 - 3500 °C, IR-CAS8CS; Chino Co., Tokyo, Japan), a spectropyrrometer⁴² (500 – 1000 nm, 1400 - 4000 °C, FAR Associates, Macedonia, OH) was used to avoid uncertainty from unknown effective sample emissivity.

2.3. High temperature X-ray diffraction

2.3.1 Quadrupole lamp furnace (QLF)^{17,33–37}

The annealed $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ powder was mixed with 10 wt% Pt powder (99.99%; Sigma-Aldrich, St Louis, MO, USA) in an agate mortar and pestle. The mixed powder was then sieved using a standard 325-mesh (45 μm), loosely packed into a sapphire capillary (SapphiT OD = 1.00 mm, ID = 0.6 mm; Crytur, Turnov, Czech Republic) and mounted in a longer alumina tube (OD = 2 mm, ID = 1.2 mm; Alfa Aesar, Inc., Ward Hill, MA). The sample was heated in air in a quadrupole lamp furnace (QLF)³³ from room temperature to a maximum of 1600 °C, in approximately 50 °C steps with a 3 min hold time at each temperature. The experiments were conducted at Beamline 33-BM-C at the Argonne National Lab, Advanced Photon Source (APS) at Argonne National Laboratory. The X-ray powder diffraction (XRPD) patterns were collected at each temperature with the Pilatus 70K detector. The sample to detector distance and wavelength were determined by means of a LaB_6 standard (SRM 660a; National Institute of Standards and Technology, Gaithersburg, MD) and were found to be 1040 mm and 0.589957 Å, respectively.

2.3.2 Conical nozzle levitator (CNL) equipped with a CO_2 laser^{19,20,50–52,32,43–49}

The $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ was processed into polycrystalline sintered spheroids, 2-3 mm in diameter, by means of a vibrating table method⁵³. Ceramic slurries were prepared from 87 vol% $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ powder having a 200 μm particle size, 5 vol% methyl cellulose binder (Sigma-Aldrich, St Louis, MO, USA), 1 vol% Darvin[®] dispersant (Vanderbilt Company, Inc., Norwalk, CT, USA) and 7 vol% water. This slurry was vibrated at a frequency of 70 Hz in a cubed-walled container having 30 mm dimensions for approximately 5 min, or until the beads had sufficient green strength. This method is described in

more detail by Santos et al.⁵³. The resulting spherical beads were heat treated at 1300 °C for 6 h at a heating rate of 2 °C/min and cooling rate of 8 °C/min.

In situ, high temperature, synchrotron XRD experiments were performed on the Hf₆Ta₂O₁₇ beads at the Advanced Photon Source (APS), Argonne National Laboratory, at Beamline 6-ID-D. Hafnium tantalate sintered beads were levitated in a stream of argon mixed with 21 % oxygen (to simulate air) in a conical nozzle levitator (CNL) system^{19,20,50–52,32,43–49}. The levitated sample rotates on axis while being heated using the beam from a 400 W sealed tube CO₂ laser (10.6 μm, Synrad FSi401SB, Mukilteo, WA, USA) beam that was partially focused on the top surface of the sample. This arrangement enabled the sample to be heated to approximately 3000 °C, which was above its melting point. The sample temperature was controlled by adjusting the incident laser beam power. A CHINO pyrometer (900 nm, 10 ms response time, 700–3500 °C, IR-CAS8CS; Chino Co., Tokyo, Japan) monitored the temperature of the bead surface incident with the laser and X-ray beam. The measured radiometric temperature was corrected using a spectral emissivity of 0.92 at the pyrometer wavelength. The CNL system setup is described in detail by Weber *et al.*⁴³. The sample was held at the desired temperature for approximately 3 minutes before taking measurements. The XRD patterns were collected at ~100 °C temperature interval by a Si Perkin Elmer XRD1621 area detector. The X-ray beam had dimensions 100 x 200 μm and was aligned so as to be incident with the laser and CHINO pyrometer before each XRPD pattern measured. The sample to detector distance and wavelength were determined with reference to a CeO₂ standard (SRM 660a; National Institute of Standards and Technology, Gaithersburg, MD, USA) and were found to be 1027.4 mm and 0.123589 Å, respectively.

2.3.3 Rietveld refinement.

The resulting XRD patterns were refined via the Rietveld method using the General Structure Analysis System Two (GSAS-II) program⁵⁴. The background, lattice constants, scale factors, atomic positions and profile functions were refined for each temperature. For the QLF system, the well-characterized thermal expansion of platinum³³ was used to accurately calculate the temperature of the powder diffraction patterns to an accuracy of ±4 °C^{33,55}. This error had two sources: (i) the variance in thermal expansion of the standard and (ii) the d-spacing resolution of the X-ray apparatus. For the CNL system, the sample temperature was recorded from the pyrometer with errors of approximately ±100 °C due to temperature gradients in the sample.

2.3.4 CNL temperature corrections

Unlike the QLF system, an internal standard has yet to be developed for the CNL system to monitor the temperature at these higher temperatures. Internal standards can be used to accurately calculate the average temperature of the diffracted volume, i.e., the volume of material being observed by X-ray diffraction. External temperature measuring devices, such as thermocouples and pyrometers may be useful for temperature control but are not so useful when internal and/or exact temperatures are required.

For example, in the CNL system the surface temperature of the levitated bead was measured by pyrometry. The incident X-ray beam needed to be located on the same top surface of the bead in order for the pyrometer to measure the temperature of the diffracting volume. During levitation, steady control of the bead height with respect to the incident X-ray beam was difficult. Upon heating, the shape of the bead could change due to thermal expansion and sintering which altered its position with respect to the incident beam. In addition, changes in aerodynamic effects can alter the sample position by as much as 100 μm , about half the height of the X-ray beam. Furthermore, these ceramic beads had relatively high temperature gradients⁵⁶ due to being heated from the top, while being cooled at the bottom^{50,51}. This is why the X-ray beam is small (200 x 100 μm) and is aligned to be incident with CO₂ laser beam on the surface of the bead. These issues could be resolved if the temperature gradient in solid samples was reduced, or if an internal standard could be used.

Since an internal standard was not available, the sample itself could be calibrated and used to estimate the temperature of the diffracted volume. This could be done by first measuring the thermal expansion using the QLF system, where the temperature accuracy was ± 4 °C, as well as by measuring the lattice parameters at a well characterized transition temperature such as the liquidus temperatures measured from thermal arrest experiments over the entire temperature composition range. Thus, lattice parameters just prior to melting could be measured and could be used as the “melting point lattice parameters”. These two data sets could then be interpolated using a polynomial fit, allowing for calculation of the temperature based on the observed lattice parameters²⁵.

This temperature correction greatly reduced uncertainty and ensured that the observed sample temperature fell within the correct temperature bounds. However, it coupled the temperature measurement with the volume measurement.

III. Results and Discussion

3.1 Liquidus, solidus and invariant transformation temperatures

The thermal arrest data in the form of cooling traces are displayed in Fig. 1 for each HfO₂-Ta₂O₅ composition. The liquidus and solidus temperatures are defined by a plateau or sudden change in temperature in the cooling trace, signifying thermal arrest. A representative cooling trace is shown in supplementary information S1, clearly demonstrating how liquidus and solidus temperatures are identified. Each composition was heated and quenched five times in order to build statistics on the liquidus and solidus points.

The average liquidus temperature and standard error as functions of composition are tabulated in Table 2. The solidus temperatures have been defined as three separate invariant transformations due to their consistency in temperature as a function of composition and have been tabulated in Table 3. However, the exact type of invariant transformation cannot be determined directly from thermal arrest experiments but could be identified using *in situ* XRD and is discussed in section 3.2. To prevent confusion, the type of invariant transformations has been listed here. The first invariant transformation is marked in green (monotectic), the second in red (eutectic) and the

third in purple (peritectic). The liquidus and invariant transformation temperatures as functions of $[\text{HfO}_2]$ mol fraction are plotted in Fig. 2.

The liquidus data collected here are similar to those collected by Turcotte et al.²² but the present data have higher resolution in composition and identify invariant transformation temperatures. We know of no other studies that mention invariant transformations in the HfO_2 - Ta_2O_5 -Temperature phase equilibria. McCormack *et al.*²⁵ recently published a more in-depth study of the $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ peritectic transformation.

3.2 Phase diagram from in-situ powder X-ray diffraction for the HfO_2 - Ta_2O_5 -temperature system

Coupling XRD with the conical nozzle levitator (CNL) system equipped with CO_2 laser, one is able to effectively map out phases *in situ* as a function of temperature. There are three key tests for equilibrium. (i) The thermodynamic parameters (S , H , V , μ_i) must be constant when the thermodynamic variables (T , P , n_i) are constant. This is achieved by ensuring that the molar volume does not change when the temperature is being held constant. (ii) When multiple phases are observed, they must satisfy the equi-partitioning of the chemical potential (i.e. the chemical potential of each component must be equal in all phases present) to ensure that the two phases are in equilibrium. This is also supported by the molar volume being constant as function of composition. (iii) The reversibility of the observed transformations.

Fig. 3 shows the phases observed in equilibrium as a function of temperature and $[\text{HfO}_2]$ mol fraction. Each triangle corresponds to the sample composition, temperature and equilibrium phases present: $\text{O-Ta}_2\text{O}_5$ with $\text{Pmm}2$ ²⁶ orthorhombic symmetry (SG 25); $\text{T-Ta}_2\text{O}_5$ with $\text{I}4_1/\text{amd}$ tetragonal symmetry (SG 141)²⁷; $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ with $\text{Ima}2$ orthorhombic symmetry (SG 46); M-HfO_2 with $\text{P}2_1/\text{c}$ monoclinic symmetry (SG 14); T-HfO_2 with $\text{P}4_2/\text{nmc}$ tetragonal symmetry (SG 137); and C-HfO_2 with $\text{Fm}\bar{3}\text{m}$ cubic symmetry (SG 225).

The constancy of the chemical potential in two phase regions can be observed in Fig 4. which shows the lattice parameters of $\text{O-Ta}_2\text{O}_5$, $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ and M-HfO_2 at room temperature. $\text{O-Ta}_2\text{O}_5$ is present within the range of $0 \leq [\text{HfO}_2] < 0.2$. Within this composition range the lattice parameters of $\text{O-Ta}_2\text{O}_5$ steadily increase, signifying the existence of a homologous series or solid solution⁵⁷. When $[\text{HfO}_2] \approx 0.2$, $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ forms. Between $0.2 \leq [\text{HfO}_2] \leq 0.8$, the lattice parameters of $\text{O-Ta}_2\text{O}_5$ and $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ are constant because these two phases are in equilibrium with each other over this composition range. $\text{O-Ta}_2\text{O}_5$ is no longer observed when $0.8 \leq [\text{HfO}_2]$. For $0.8 \leq [\text{HfO}_2] \leq 0.888$, the lattice parameters of $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ vary as a function of composition, signifying another homologous series or solid solution⁵⁷. When $0.888 \leq [\text{HfO}_2]$, $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ and M-HfO_2 are observed. For $0.888 \leq [\text{HfO}_2] \leq 1$ the lattice parameters of $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ and M-HfO_2 are observed to be constant, as expected for a two-phase regime in equilibrium.

The “solid solution” like ranges for $\text{O-Ta}_2\text{O}_5$ and $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ probably a homologous series of closely spaced phases rather than true a solid solution. That is, as HfO_2 is added to $\text{O-Ta}_2\text{O}_5$ or when the Hf/Ta ratio is changed in the compound $\text{Hf}_6\text{Ta}_2\text{O}_{17}$, a series of related ordered structures form. This is indicated because satellite low intensity peaks appear and disappear as the composition is changed. Determining which satellite peaks appear and disappear as a function of composition is

difficult for X-ray powder diffraction due to the large scattering factors of Hf and Ta compared to that of O^{58,59}. The small contribution of oxygen to the total scattering obscures slight symmetry changes which may be caused by oxygen ordering. It is clear that these structures are related, as the high intensity peaks (predominantly scattering from Hf/Ta) change d-spacing continuously as a function of composition, suggesting that cation sublattice is essentially the same for both the O-Ta₂O₅ homologous series as well as the Hf₆Ta₂O₁₇ homologous series. McCormack et al.²⁴ have proposed how the Hf₆Ta₂O₁₇ structure can accommodate a $0.8 \leq [\text{HfO}_2] \leq 0.888$ change in composition via movements of O and changes in superstructure multiplicity. Although the O-Ta₂O₅ at room temperature exhibits a homologous series, when it transforms to T-Ta₂O₅ it becomes a solid solution. This is because there is an observed change in lattice parameter as HfO₂ is added to T-Ta₂O₅ and there is no appearance of satellite peaks.

The phase transformations observed in the phase diagram (Fig. 4) are summarized in Table 4 with their associated changes in molar volume at temperature. Several transformations need to be verified and tested for reversibility to ensure that they are in fact the equilibrium transformations. These include:

- (i) the first invariant transformation (monotectic: $L \rightleftharpoons \text{T-Ta}_2\text{O}_5 + L_1$)
- (ii) the second invariant transformation (eutectic: $L \rightleftharpoons \text{T-Ta}_2\text{O}_5 + \text{O-Hf}_6\text{Ta}_2\text{O}_{17}$),
- (iii) the third invariant transformation (peritectic: $\text{HfO}_2 + L \rightleftharpoons \text{Hf}_6\text{Ta}_2\text{O}_{17}$),
- (iv) the $\text{O-Ta}_2\text{O}_5 \rightleftharpoons \text{T-Ta}_2\text{O}_5$ transformation and the eutectoidal transformation: $\text{T-Ta}_2\text{O}_5 \rightleftharpoons \text{O-Ta}_2\text{O}_5 + \text{O-Hf}_6\text{Ta}_2\text{O}_{17}$

The first invariant transformation can be identified as a monotectic transformation based on two key observations: (i) It is confirmed that no solid phase exists above the first invariant transformation temperature spanning its composition range and signifying two possible invariant transformations: monotectic or syntectic. (ii) It is confirmed that the pure end member (Ta₂O₅) has a melting point higher than the first invariant transformation temperature. This is characteristic of a monotectic and not a syntectic invariant transformation, so that the first invariant transformation is most likely monotectic. This monotectic transformation was observed to be reversible above and below the monotectic transformation temperature as depicted in supplementary information (S3). Due to the rarity of monotectic transformations, what is required for confirmation is a clear observation of the two-phase liquid region in equilibrium. Unfortunately, quenching the sample within the proposed two-phase liquid regime did not reveal immiscible liquid microstructural features, either because they were not kinetically trapped or because it does not exist. It is expected that an *in-situ* scattering technique such as small-angle X-ray scattering (SAXS) would be required to confirm the immiscible liquid region.

The second invariant transformation can be identified as a eutectic by examining the liquid-solid two-phase regions. The *in situ* XRD was able to confirm that, above the second invariant transformation temperature for ($0.3 \leq [\text{HfO}_2]$), liquid was observed to co-exist in equilibrium with T-Ta₂O₅. However, when above the second invariant transformation temperature, for ($[\text{HfO}_2] \leq 0.4$), liquid existed in equilibrium with O-Hf₆Ta₂O₁₇. This suggests that the eutectic temperature is at $0.3 \leq [\text{HfO}_2] \leq 0.4$. It is estimated from extrapolation that the eutectic composition occurs at $[\text{HfO}_2] \approx 0.33$. This eutectic transformation is reversible above and below the eutectic

transformation temperature for a hypo-eutectic composition (S4) and a hyper-eutectic composition (S5).

The third invariant transformation can be identified as a peritectic by the observed decomposition of the $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ phase into T-HfO_2 and liquid. The $\text{O-Hf}_6\text{Ta}_2\text{O}_{17} \rightleftharpoons \text{T-HfO}_2 + \text{L}$ peritectic was observed to be reversible at temperature (S6). This transformation has been studied in depth and is published elsewhere by McCormack *et al.*²⁵ and thus will not be discussed further here.

The equilibrium structure of room temperature $\text{O-Ta}_2\text{O}_5$ was the most difficult to determine. This stemmed from the difficulty in verifying reversibility of the $\text{O-Ta}_2\text{O}_5 \rightleftharpoons \text{T-Ta}_2\text{O}_5$ transformation. It is clear that the room temperature $\text{O-Ta}_2\text{O}_5$ phase transforms to the $\text{T-Ta}_2\text{O}_5$ phase. However, on cooling, a $\text{M}'\text{-Ta}_2\text{O}_5$ (monoclinic - I2^{27} (SG 5)) and an $\text{O}'\text{-Ta}_2\text{O}_5$ (orthorhombic - Imma^{27} (SG 74)) phase form. These phases did not revert back to $\text{O-Ta}_2\text{O}_5$ on the time scale of the *in situ* diffraction experiment. It took 40 hours annealing in a box furnace at 1200°C for the $\text{T-Ta}_2\text{O}_5$, $\text{M}'\text{-Ta}_2\text{O}_5$ and $\text{O}'\text{-Ta}_2\text{O}_5$ phases to revert back to the equilibrium $\text{O-Ta}_2\text{O}_5$ phase (S7). This shows that the $\text{O-Ta}_2\text{O}_5 \rightleftharpoons \text{T-Ta}_2\text{O}_5$ transformation is reversible, containing metastable forward transformations on cooling from the high temperature $\text{T-Ta}_2\text{O}_5$ phase. It is proposed that the metastable phases formed on cooling of $\text{T-Ta}_2\text{O}_5$ follow: $\text{T-Ta}_2\text{O}_5 \rightarrow \text{M}'\text{-Ta}_2\text{O}_5 \rightarrow \text{O}'\text{-Ta}_2\text{O}_5 \rightarrow \text{O-Ta}_2\text{O}_5$. This is based on the temperatures at which the metastable Ta_2O_5 begin to form: $\text{M}'\text{-Ta}_2\text{O}_5$ at $T \approx 960^\circ\text{C}$ and $\text{O}'\text{-Ta}_2\text{O}_5$ at $T \approx 320^\circ\text{C}$ which are similar to what has been previously reported in the literature²⁷. The metastable transformations in Ta_2O_5 need to be studied more rigorously.

This transformational reversibility of $\text{T-Ta}_2\text{O}_5 \rightleftharpoons \text{O-Ta}_2\text{O}_5$ was consistent across the entire composition range where $\text{T-Ta}_2\text{O}_5$ was stable, thus confirming the reversibility of the eutectoidal transformation $\text{T-Ta}_2\text{O}_5 \rightleftharpoons \text{O-Ta}_2\text{O}_5 + \text{O-Hf}_6\text{Ta}_2\text{O}_{17}$. The exact composition and temperature of the eutectoidal transformation needs to be verified. The transformation has not been directly observed in the microstructure when quenching from the liquid phase in the hyper-eutectoidal regime. The latent heat from the eutectoidal transformation was not observed in cooling trace experiments. Although there is little evidence for the eutectoidal transformation based on the data collected, it must exist in the $\text{HfO}_2\text{-Ta}_2\text{O}_5$ phase diagram at low $[\text{HfO}_2]$ mol fractions to ensure that the Gibbs Phase Rule⁶⁰ is satisfied.

The M-HfO_2 to T-HfO_2 transformation¹⁷ and the T-HfO_2 to C-HfO_2 transformation¹⁸ have been shown to be reversible and thus will not be discussed in more detail here. It was observed, that C-HfO_2 existed in equilibrium with liquid when $[\text{HfO}_2] = 0.95$.

The phase diagram can be seen more clearly without data points in Fig. 5. It must be stressed that this preliminary phase diagram has not been built based on minimizing the Gibbs free energy. It has been constructed based on *in situ* equilibrium phase identification (according to equipartitioning of chemical potential and transformational reversibility) and the Gibbs Phase Rule⁶⁰. While the identification of equilibrium phases is of utmost importance for accurate phase equilibria, one also needs the Gibbs free energy for each equilibrium phase, which should be attainable by the CALPHAD computational method in the future. The homologous series lines drawn in the $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ regime match those predicted by the work of McCormack and Kriven²⁴ and Roth *et al.*⁶¹ The homologous series lines are drawn for the Ta_2O_5 regime are simply a schematic and have not been

determined experimentally or theoretically in this work. The line compositions of the Ta₂O₅ homologous series still need to be determined.

3.3 Molar volumes of equilibrium phases

X-ray powder diffraction (XRPD) can be used to calculate the molar volume per cation of phases using Rietveld refinement according to $\bar{V} = \frac{V_{\text{cell}}}{N_{\text{C}}Z}$, where \bar{V} is the molar volume, V_{cell} is the volume of the unit cell, N_{C} is the number of cations in the formula unit and Z is the formula unit per unit cell. Therefore, $N_{\text{C}}Z$ is the cation formula unit. The molar volumes as a function of temperature and composition for the equilibrium phases within the HfO₂-Ta₂O₅-Temperature phase space are plotted below and tabulated in the supplementary information (S8, S9, S10, S11).

Fig. 6 depicts the molar volume as function of [HfO₂] mol fraction for the three equilibrium structures at room temperature. There is a large change in molar volume of $\frac{\Delta\bar{V}}{\bar{V}} = -25.24\%$ when comparing O-Ta₂O₅ and O-Hf₆Ta₂O₁₇, which has been verified from bulk pycnometer density measurements. There is a small change in molar volume of $\frac{\Delta\bar{V}}{\bar{V}} = 3.07\%$ when comparing O-Hf₆Ta₂O₁₇ and M-HfO₂.

Fig. 7 displays the molar volume as a function of temperature for the Ta₂O₅ compounds. The molar volume of O-Ta₂O₅ increases, following a second-order polynomial as expected. At around 1360 °C, there is a phase transition from the orthorhombic Pmm2 (SG 25) symmetry to tetragonal I4₁/amd (SG 141) symmetry, along with a first order transformation which is accompanied by an associated $\frac{\Delta\bar{V}}{\bar{V}} = -2.32\%$. The molar volume of the T-Ta₂O₅ phase then increases almost linearly as a function of temperature up until melting at approximately 1860 °C. The thermal expansion and transformation mechanisms will be discussed in more detail in a future publication.

Fig. 8 shows the molar volume as function of temperature for the Hf₆Ta₂O₁₇ compound. The molar volume of O-Hf₆Ta₂O₁₇ increases in a sigmoidal manner as function of temperature up to the peritectic temperature 2250 °C. At the transformation temperature there is a crystallographic molar volume change of $\frac{\Delta\bar{V}}{\bar{V}} = 1.6\%$ between the O-Hf₆Ta₂O₁₇ and the T-HfO₂ phase. The T-HfO₂ formed from the peritectic transformation is observed to undergo complete melting at around ~2450 °C. The thermal expansion and transformation mechanisms of this peritectic transformation are discussed in more detail by McCormack et al.²⁵ elsewhere.

Fig. 9 shows the molar volume as a function of temperature for the HfO₂ compound. The molar volume of M-HfO₂ increases according to a second order polynomial. On heating, M-HfO₂ goes through a first order transformation from monoclinic P2₁/c (SG 14) to tetragonal P4₂/nmc (SG 137) symmetry at 1715 °C with an associated change in volume $\frac{\Delta\bar{V}}{\bar{V}} = -2.78\%$. As the temperature of T-HfO₂ increases further, it undergoes a first order transformation from tetragonal P4₂/nmc (SG 137) to cubic Fm $\bar{3}$ m (225) symmetry with a volume change of $\frac{\Delta\bar{V}}{\bar{V}} \approx 0\%$. The thermal expansion and transformation mechanisms are discussed in more detail by Haggerty *et al.*¹⁷ and by Tobase *et al.*¹⁸.

IV. Conclusions

The previously unknown experimental $\text{HfO}_2\text{-Ta}_2\text{O}_5$ -temperature phase diagram has been elucidated up to 3400 °C using a quadrupole lamp furnace and conical nozzle levitator system equipped with a CO_2 laser, in conjunction with synchrotron X-ray powder diffraction. These in-situ techniques allowed for the determination of: (i) liquidus, solidus and invariant transformation temperatures as a function of composition from thermal arrest experiments, (ii) determination of equilibrium phases through testing of the reversibility condition via in-situ X-ray diffraction, (iii) molar volume measurements as a function of temperature for equilibrium phases. From this data, an experimental $\text{HfO}_2\text{-Ta}_2\text{O}_5$ phase diagram was been constructed based on the Gibbs Phase Rule⁶⁰.

The thermal arrest experiments and in-situ X-ray diffraction experiments led to the identification of four invariant transformations: (i) a monotectic, that still needs to be verified directly using Small Angle X-ray Scattering (SAXS), (ii) a eutectic, (iii) a peritectic and (iv) a eutectoid, that is expected based on the Gibbs Phase Rule⁶⁰. This eutectoid still needs to be verified directly.

Supplementary Information

Additional supplementary information can be found on the online version of this article:

S1: Representative cooling trace showing how the liquidus and solidus are determined from cooling trace data

S2: Tabulated room temperature lattice parameters as function of $[\text{HfO}_2]$ composition for $\text{O-Ta}_2\text{O}_5$, $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ and M-HfO_2

S3: Reversibility of the monotectic invariant based on in-situ X-ray diffraction.

S4: Reversibility of the hypo-eutectic invariant based on in-situ X-ray diffraction.

S5: Reversibility of the hyper-eutectic invariant based on in-situ X-ray diffraction.

S6: Reversibility of the peritectic invariant based on in-situ X-ray diffraction.

S7: Reversibility of the orthorhombic Ta_2O_5 to tetragonal Ta_2O_5 transformation based on ex-situ X-ray diffraction.

S8: Tabulated molar volume as a function of HfO_2 composition for $\text{O-Ta}_2\text{O}_5$, $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ and M-HfO_2 .

S9: Tabulated molar volume of Ta_2O_5 as a function of temperature.

S10: Tabulated molar volume of $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ as a function of temperature.

S11: Tabulated molar volume of HfO_2 as a function of temperature.

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Figures

Fig. 1. Cooling trace curves collected on $\text{HfO}_2\text{-Ta}_2\text{O}_5$. five samples of each composition were tested to determine the recalescence temperature (liquidus) and invariant reaction temperatures.

Fig. 2. Liquidus temperatures and invariant reaction temperatures: (i) Monotectic ($L_1 \rightleftharpoons \alpha + L_2$), (ii) Eutectic ($L \rightleftharpoons \alpha + \beta$) and (iii) Peritectic ($\alpha + L \rightleftharpoons \beta$), plotted as function of $[\text{HfO}_2]$ (mol fraction) in Ta_2O_5 .

Fig. 3. Construction of the $\text{HfO}_2\text{-Ta}_2\text{O}_5$ -Temperature phase space from in-situ X-ray powder diffraction. Each triangle corresponds to the sample composition, temperature and the observed equilibrium phases. The observed equilibrium phases correspond to the color of the triangle's corners. The left corner refers to Ta_2O_5 (black: orthorhombic, red: tetragonal, white: not present), the top refers to $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ (black: orthorhombic, white: not present) the right corner refers to HfO_2 (black: monoclinic, red: tetragonal, blue: cubic, white: not present) and the center refers to liquid (black: present, white: not present). These data points were collected using the conical nozzle levitator system (CNL).

Fig. 4. Lattice parameters of the $\text{O-Ta}_2\text{O}_5$, $\text{O-Hf}_6\text{Ta}_2\text{O}_{17}$ and M-HfO_2 compounds as a function of HfO_2 mol fraction $[\text{HfO}_2]$ at room temperature. Grey signifies a homologous series regime while white signifies a two-phase regime. This data is tabulated in supplementary information S2.

Fig. 5. HfO₂-Ta₂O₅-Temperature phase space built based on the observed equilibrium phases from in-situ X-ray powder diffraction and the Gibbs Phase Rule. The H subscript is referring to the compounds which exhibit a homologous series. The dashed lines in the O-Ta₂O₅ and the O-Hf₆Ta₂O₁₇ regime signify the potential homologous series of compounds. The eutectoid and peritectic tie lines would have to be adjusted based on the Gibbs Phase Rule to accommodate the homologous series. The homologous series lines drawn in the Hf₆Ta₂O₁₇ regime matches that predicted by the work of McCormack and Kriven²⁴ and Roth et al.⁶¹ The homologous series lines drawn for the Ta₂O₅ regime are simply a schematic and have not been determined experimentally or theoretically.

Fig. 6. Molar volume of the O-Ta₂O₅, O-Hf₆Ta₂O₁₇ and M-HfO₂ as function of HfO₂ mol fraction [HfO₂] at room temperature. The large change in molar volume ($(\Delta V)/V = -25.24\%$) between O-Ta₂O₅ and O-Hf₆Ta₂O₁₇ has been verified from pycnometer density measurements. The molar volume change between the equilibrium O-Hf₆Ta₂O₁₇ and M-HfO₂ structures is $(\Delta V)/V = 3.07\%$. Grey signifies a homologous series regime while white signifies a two-phase regime. This data is tabulated in supplementary information S8.

Fig. 7. Molar volume of O-Ta₂O₅ and T-Ta₂O₅ as function of temperature. Note the first order transformation at $T \approx 1350^\circ\text{C}$ with an associated molar volume change of $(\Delta V)/V = -2.32\%$. Complete melting was observed at $T \approx 1870^\circ\text{C}$. Grey signifies data collected using the CNL system while white signifies data collected using the QLF system. This data is tabulated in supplementary information S9. Atomic mechanisms for the anisotropic thermal expansion related to this molar volume change will be discussed in more detail in a future paper.

Fig. 8. Molar volume of O-Hf₆Ta₂O₁₇ and T-HfO₂ as function of temperature. Note the peritectic transformation at $T \approx 2244^\circ\text{C}$ with an associated crystallographic molar volume change of $(\Delta V)/V = 1.16\%$. This change in volume does not include the volume of the liquid phase. $T \approx 2450^\circ\text{C}$. Grey signifies data collected using the CNL system while white signifies data collected using the QLF system. This data is tabulated in supplementary information S10. Atomic mechanisms for the anisotropic thermal expansion related to this molar volume change and the peritectic transformation is discussed in more depth by McCormack et al.²⁵

Fig. 9. Molar volume of HfO₂ as function of temperature. Note the first order transformation from M-HfO₂ to T-HfO₂ at $T \approx$ with an associated molar volume change of $(\Delta V)/V = -2.78\%$. Also note the second order transformation from T-HfO₂ to C-HfO₂ at $T \approx 2600^\circ\text{C}$ with an associated molar volume change of $(\Delta V)/V \approx 0$. $T \approx 1700^\circ\text{C}$. Grey signifies data collected using the CNL system while white signifies data collected using the QLF system. This data is tabulated in supplementary information S11. Atomic mechanisms for the anisotropic thermal expansion related to this molar volume change is discussed in more depth by Haggerty et al.¹⁷

Tables

Table 1 – Summary of HfO₂-Ta₂O₅ binary samples fabricated using the steric entrapment method. Composition error (XRF) comes from the ability to deconvolute and quantify the Hf and Ta similar characteristic X-rays. Phase fraction error (synchrotron X-ray diffraction) comes from the ability to resolve phase peaks and intensities.

Sample	Composition (mol fraction)		XRF (mol fraction) ±0.01		Phases (mass fraction at room temperature) ±0.03		
	[HfO ₂]	[Ta ₂ O ₅]	[HfO ₂]	[Ta ₂ O ₅]	HfO ₂	Ta ₂ O ₅	Hf ₆ Ta ₂ O ₁₇
Ta ₂ O ₅	0.00	1.00	0.00	1.00	0.00	1.00	0.00
0.05HfO ₂ 0.95Ta ₂ O ₅	0.05	0.95	0.05	0.95	0.00	1.00	0.00
0.1HfO ₂ 0.9Ta ₂ O ₅	0.10	0.90	0.12	0.88	0.00	1.00	0.00
0.15HfO ₂ 0.85Ta ₂ O ₅	0.15	0.85	0.15	0.85	0.00	1.00	0.00
0.2HfO ₂ 0.8Ta ₂ O ₅	0.20	0.80	0.23	0.77	0.00	0.82	0.18
0.3HfO ₂ 0.7Ta ₂ O ₅	0.30	0.70	0.31	0.69	0.00	0.52	0.48
0.4HfO ₂ 0.6Ta ₂ O ₅	0.40	0.60	0.40	0.60	0.00	0.35	0.65
0.5HfO ₂ 0.5Ta ₂ O ₅	0.50	0.50	0.50	0.50	0.00	0.23	0.77
0.6HfO ₂ 0.4Ta ₂ O ₅	0.60	0.40	0.60	0.40	0.00	0.13	0.87
0.7HfO ₂ 0.3Ta ₂ O ₅	0.70	0.30	0.72	0.28	0.00	0.09	0.91
0.8HfO ₂ 0.2Ta ₂ O ₅	0.80	0.20	0.77	0.23	0.00	0.03	0.97
Hf ₆ Ta ₂ O ₁₇	0.86	0.14	0.86	0.14	0.00	0.00	1.00
0.9HfO ₂ 0.1Ta ₂ O ₅	0.90	0.10	0.90	0.10	0.02	0.00	0.98
0.95HfO ₂ 0.05Ta ₂ O ₅	0.95	0.05	0.96	0.04	0.48	0.00	0.52
HfO ₂	1.00	0.00	1.00	0.00	1.00	0.00	0.00

Table 2 – Liquidus temperatures

Composition [HfO ₂] (mol fraction)	Liquidus Temperature (°C)
0.00	1877 ± 40
0.05	1952 ± 39
0.12	2007 ± 33
0.15	1941 ± 35
0.23	1887 ± 37
0.31	1848 ± 40
0.4	1845 ± 43
0.5	1925 ± 33
0.6	2013 ± 43
0.72	2070 ± 33
0.77	2250 ± 43
0.86	2450 ± 40
0.9	2640 ± 40
0.96	2733 ± 33
1.00	2758 ± 33

Table 3 – Invariant Transformation/Reactions.

Invariant point	Composition [HfO ₂] (mol fraction)	Temperature (°C)
First invariant: Monotectic (L ₁ ⇌ T-Ta ₂ O ₅ + L ₂)	0.00 < [HfO ₂] < 0.05	1824 ± 36
Second invariant: Eutectic (L ⇌ T-Ta ₂ O ₅ + O-Hf ₆ Ta ₂ O ₁₇)	[HfO ₂] ≈ 0.33 ± 0.03	1731 ± 34
Third invariant: Peritectic T-HfO ₂ + L ⇌ O-Hf ₆ Ta ₂ O ₁₇)	[HfO ₂] ≈ 0.84 ± 0.03	2244 ± 37
Fourth invariant: Eutectoid* (T-Ta ₂ O ₅ ⇌ O-Ta ₂ O ₅ + O-Hf ₆ Ta ₂ O ₁₇)	[HfO ₂] ≈ 0.24*	~1300*

*The eutectoid point was not directly determined. It is included here as it is required to satisfy the Gibbs Phase Rule. The presented composition and temperatures are estimates.

Table 4 – Change in molar volume for transformations in the HfO₂-Ta₂O₅-Temperature system with reference to Figs. 6-9

Transformation/Reaction	Change in Molar Volume (%)	Temperature (°C)
O-Ta ₂ O ₅ + M-HfO ₂ ⇌ O-Hf ₆ Ta ₂ O ₁₇ * (O-Ta ₂ O ₅ compared to O-Hf ₆ Ta ₂ O ₁₇)	$\frac{\Delta \bar{V}}{V} = -25.24$	~26*
O-Hf ₆ Ta ₂ O ₁₇ ⇌ M-HfO ₂ + O-Ta ₂ O ₅ * (O-Hf ₆ Ta ₂ O ₁₇ compared to M-HfO ₂)	$\frac{\Delta \bar{V}}{V} = 3.07$	~26*
O-Ta ₂ O ₅ ⇌ T-Ta ₂ O ₅	$\frac{\Delta \bar{V}}{V} = -2.32$	~1350
O-Hf ₆ Ta ₂ O ₁₇ ⇌ T-HfO ₂ + L	$\frac{\Delta \bar{V}}{V} = 1.16^{**}$	~2244
M-HfO ₂ ⇌ T-HfO ₂	$\frac{\Delta \bar{V}}{V} = -2.78$	~1700
T-HfO ₂ ⇌ C-HfO ₂	$\frac{\Delta \bar{V}}{V} \approx 0$	~2600

* These are reactions comparing the change in molar volume as function of [HfO₂] at room temperature. Refer to Fig 6.

** Change in molar volume for crystallographic phases (does not include volume of liquid phase).















