Combining computational and experimental investigation of high temperature thermodynamics and structure of cubic ZrO$_2$ and HfO$_2$

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Structure and thermodynamics of pure cubic ZrO$_2$ and HfO$_2$ were studied computationally and experimentally from their tetragonal to cubic transition temperatures ($2311$ and $2530$ °C) to their melting points ($2710$ and $2800$ °C). Computations were performed using automated ab initio molecular dynamics techniques. High temperature synchrotron X-ray diffraction on laser heated aerodynamically levitated samples provided experimental data on volume change during tetragonal-to-cubic phase transformation ($0.55 \pm 0.09\%$ for ZrO$_2$ and $0.87 \pm 0.08\%$ for HfO$_2$), density and thermal expansion. Fusion enthalpies were measured using drop and catch calorimetry on laser heated levitated samples as $55 \pm 7$ kJ/mol for ZrO$_2$ and $61 \pm 10$ kJ/mol for HfO$_2$, compared with $54 \pm 2$ and $52 \pm 2$ kJ/mol from computation. Volumetric thermal expansion for cubic ZrO$_2$ and HfO$_2$ is similar and reach $(4 \pm 1) \cdot 10^{-5}/K$ from experiment and $(5 \pm 1) \cdot 10^{-5}/K$ from computation. An agreement with experiment renders confidence in values obtained exclusively from computation: namely heat capacity of cubic HfO$_2$ and ZrO$_2$, volume change on melting, and thermal expansion of the liquid to $3127$ °C. Computed oxygen diffusion coefficients indicate that above $2400$ °C pure ZrO$_2$ is an excellent oxygen conductor, perhaps even better than YSZ.

Hafnium and zirconium oxides are indispensable constituents for development of the formulations for structural ceramics$^1$, thermal barrier coatings$^2$, high temperature refractories$^3$ and for nuclear applications, such as matrices for fission and transmutation and sacrificial materials for core catchers for next generation nuclear reactors$^4$. ZrO$_2$ and HfO$_2$ are isostructural and exhibit monoclinic-tetragonal-cubic transformations before melting at $2710$ and $2800$ °C, respectively. Thermodynamic assessments for pure oxides to the melting temperatures are required for prediction of phase composition, stability, and microstructure in multicomponent systems using Calphad type$^5$ approaches, which have proven to be extremely useful in metallurgy and ceramics.

The latest review of experimental data and assessment of the Gibbs free energy functions for all HfO$_2$ and ZrO$_2$ phases was performed by Wang, Zinkevich and Aldinger in 2006$^6$ (referred further as the WZA assessment). It was adopted by most researchers for Calphad modeling for ZrO$_2$- and HfO$_2$- containing systems$^2,7$. A plethora of computational and experimental investigations has been devoted to the thermodynamics of monoclinic and tetragonal phases$^8,9$, and the structure of the liquid was studied experimentally and computationally$^{10,11}$. However, for the cubic phases we only know unambiguously that they are stable for a few hundred degrees before melting and have unit cell parameters somewhere between $5.1$ and $5.3$ Å$^{12}$. Measurements of enthalpy increments for cubic ZrO$_2$ and HfO$_2$ phases were performed by Pears et al. in 1963$^{13}$. However, their samples were exposed to carbon vapor in a graphite furnace and their data were not used in the WZA assessment$^6$. The value for ZrO$_2$ fusion enthalpy ($87$ kJ/mol) reported in the JANAF tables$^{14}$ and used by WZA$^6$ can be traced$^{15}$ to an assessment made by Kelley in 1936$^{16}$ based on the slope of the solidus in early ZrO$_2$-SiO$_2$ and ZrO$_2$-MgO phase diagrams.

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3.669 ± 0.003 Å, and this uncertainty has been propagated to experimental density and thermal ± values for volumetric thermal expansion are in good agreement with computations and within 4 (± agreement with experiment with differences less than 0.5%. After propagation of uncertainties, the experimental well as ensuring proper modeling of all forms of excited states (defect formation and diffusion, potential anharmonic large system sizes and sufficiently long simulation times while still using accurate electronic structure calculations as as lie in thermal gradients unavoidable in conditions of uniaxial laser heating of aerodynamically levitated samples used for calorimetry17,18 and X-ray diffraction19–21. On the computational side, the difficulties reside in reaching sufficiently between computed and measured values for fusion enthalpies and for thermal expansion supports the validity of the transition from the tetragonal phase were measured by high temperature X-ray diffraction experiments. The agreement thus, we conclude that no direct experimental measurements of fusion enthalpy for ZrO2 and HfO2 have been performed to date. In this work, we sought to fill this gap in the available data by measuring and computing the fusion enthalpies of ZrO2 and HfO2. The combination of experimental and computational method offers a unique opportunity for corroboration that is essential given the challenges associated with each approach. On the experimental side, the difficulties lie in thermal gradients unavoidable in conditions of uniaxial laser heating of aerodynamically levitated samples used for calorimetry17,18 and X-ray diffraction19–21. On the computational side, the difficulties reside in reaching sufficiently large system sizes and sufficiently long simulation times while still using accurate electronic structure calculations as well as ensuring proper modeling of all forms of excited states (defect formation and diffusion, potential anharmonic phonons and electron excitations). Thermal expansions of cubic ZrO2 and HfO2, and volume change during the transition from the tetragonal phase were measured by high temperature X-ray diffraction experiments. The agreement between computed and measured values for fusion enthalpies and for thermal expansion supports the validity of the heat capacities, diffusion coefficients, and volume change upon melting obtained from the computation. Results and Discussion A summary of the results of ab initio computations is presented in Table 1 and Fig. 1. Results from high temperature X-ray diffraction are tabulated in Supplementary Information. Below, the thermodynamic data for cubic ZrO2 and HfO2 from computation and experiment are discussed together in the same order as in Tables 2 and 3 and are compared with literature values.

Tetragonal - cubic transition and thermal expansion of cubic phases. Temperatures for tetragonal-cubic transition and melting points for ZrO2 and HfO2 were accepted from the WZA assessment and were used in this work for the evaluation of the temperature of the diffraeted volume of the laser heated samples. Cubic ZrO2 and HfO2 have a fluorite structure with space group Fm3m and 4 formula units per cell (Z = 4). Besides the mineral fluorite (CaF2), which gives the name for the structure type, natural and synthetic uraninite (UO2), thorianite (ThO2), and cerianite (CeO2) are found in this structure. Thermophysical properties of UO2 and ThO2 above 2000 °C were studied extensively for nuclear reactors safety assessments22,23, and a comparison of the high temperature structures for UO2 with ZrO2 and HfO2 from this work is given at the end of this paper. In the tetragonal (P4/2/mmc, Z = 2) and cubic phases, Zr and Hf are coordinated by eight oxygen atoms, but in the monoclinic structure (P21/c), stable at room temperature, the cation coordination is 7. Unit cell parameters of the tetragonal and cubic phases of ZrO2 and HfO2 at transition temperatures were refined from XRD patterns containing both phases (Fig. 2), giving volume change upon transition. There are a number of values in the ICSD database24 for volumes of stable and metastable tetragonal ZrO2 at temperatures below 1627 °C (see Supplementary Information). Our value for the volume of tetragonal ZrO2 at the transition temperature is consistent with the trend of close to linear volume expansion of the tetragonal phase, yielding an average value for of volumetric thermal expansion (αv) of 3.9·10−5 K−1 in the 300–2311 °C range.

| T, °C | CPU Hours | MD length, ps | Volume, Å3/atom | Energy, eV/atom | HSE P correction, kBar | HSE E correction, eV/atom | α, Å | Density, g·cm−3 |
|-------|-----------|---------------|----------------|----------------|------------------------|--------------------------|------|----------------|
| Cubic ZrO2 | 2327 | 10600 | 15 | 12.32 (2) | −8.829 (5) | −52.02 | −1.97 | 5.288 (2) | 5.54 (1) |
| | 2527 | 26000 | 34 | 12.43 (2) | −8.761 (4) | −51.19 | −1.97 | 5.303 (2) | 5.49 (1) |
| | 2627 | 26500 | 34 | 12.50 (2) | −8.720 (4) | −50.83 | −1.97 | 5.313 (2) | 5.46 (1) |
| | 2727 | 11200 | 14 | 12.54 (2) | −8.687 (4) | −51.08 | −1.96 | 5.320 (2) | 5.44 (1) |
| Liquid ZrO2 | 2827 | 29300 | 31 | 14.03 (5) | −8.490 (4) | −44.45 | −1.93 | 4.86 (2) | |
| | 2927 | 29300 | 31 | 14.16 (4) | −8.456 (4) | −43.91 | −1.92 | 4.82 (1) | |
| | 3127 | 29600 | 28 | 14.39 (4) | −8.383 (4) | −43.45 | −1.92 | 4.74 (1) | |
| Cubic HfO2 | 2527 | 19200 | 62 | 11.96 (1) | −9.346 (4) | −59.05 | −1.98 | 5.235 (2) | 9.74 (1) |
| | 2627 | 19200 | 59 | 12.00 (1) | −9.306 (4) | −59.34 | −1.98 | 5.242 (2) | 9.71 (1) |
| | 2727 | 7800 | 23 | 12.08 (2) | −9.264 (6) | −58.84 | −1.98 | 5.253 (2) | 9.65 (1) |
| Liquid HfO2 | 2827 | 21500 | 56 | 13.35 (5) | −9.068 (4) | −51.89 | −1.95 | 8.73 (3) | |
| | 2927 | 21800 | 56 | 13.40 (5) | −9.038 (4) | −51.46 | −1.94 | 8.69 (3) | |
| | 3127 | 22800 | 55 | 13.66 (4) | −8.963 (7) | −51.36 | −1.94 | 8.53 (2) | |
We did not locate any previous reports on experimental or computational values for the thermal expansion. There are few reported values for the cell parameters of high temperature cubic ZrO$_2$ and HfO$_2$ and all of them were measured in vacuum and thus on possibly somewhat reduced samples. In fact, even though cubic ZrO$_2$ was assumed in the early phase diagrams by Kelley$^{16}$ in 1936 for the assessment of the fusion enthalpy, the existence of pure cubic phases at high temperature was still questioned in 1962$^{25}$, due to the lack of structural data in oxidizing conditions. Boganov et al.$^{26}$ studied high temperature transformations in ZrO$_2$ and HfO$_2$ in a vacuum of 5·10$^{-6}$ Torr with heating by the electron beam and reported the unit cell parameter for ZrO$_2$ as 5.256(3) Å at 2330 °C and for HfO$_2$ as 5.30(1) Å at ~2700–2750 °C. The latter value for cubic HfO$_2$ was cited in reviews by Glushkova$^{27}$ and Wang$^{12}$. Considering experimental conditions, these values probably refer to oxygen deficient cubic ZrO$_2^{−x}$ and HfO$_2^{−x}$, known to exist in Zr-O and Hf-O systems$^{28}$, and thus the differences with the results of our work are expected. Passerini$^{29}$ derived room temperature cell parameters for cubic ZrO$_2$ and HfO$_2$ as 5.065 Å and 5.115 Å by extrapolation from their fluorite solid solutions with CeO$_2$. Combining his values with cell parameters before melting from this work (5.291 and 5.265 Å) gives an average volumetric thermal expansion from room temperature to the melting points of ~5·10$^{-5}$ K$^{-1}$ for ZrO$_2$ and ~3·10$^{-5}$ K$^{-1}$ for HfO$_2$.

Volume change upon melting, density and thermal expansion of liquid ZrO$_2$ and HfO$_2$. At 25 °C, our computation gives volume of monoclinic ZrO$_2$ and HfO$_2$ as 35.22 and 34.11 Å$^3$ per formula unit, respectively. This compares well with experimental values of 35.15 and 34.57 Å$^3$ per formula unit by Hann$^{30}$. The density change of cubic ZrO$_2$ and HfO$_2$ with temperature from high temperature XRD data is shown in Tables $2$ and $3$ and Fig. $3$ and compared with the results from computations. The good agreement allows us to rely on $ab$ initio MD results for volume change upon melting as well as density and thermal expansion of the liquid phases. ZrO$_2$ and HfO$_2$ show similar expansion upon melting, 11 ± 2% and 10 ± 2%, respectively. For the temperature range sampled by computation, volumetric thermal expansions of liquid ZrO$_2$ and HfO$_2$ fall within (8 ± 1)·10$^{-5}$ – twice that for the cubic phase. Despite known biases in the lattice parameters calculated via DFT methods$^{31}$, calculated volume changes tend to be much more accurate, due to systematic error cancellations.
Density of liquid HfO$_2$ was refined from PDF measurements by Gallington et al. 8.73–8.53 g/cm$^3$ at 2827–3127 °C from our computations.

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Enthalpy and entropy of fusion. Ab initio MD computations resulted in values for fusion enthalpies of ($\Delta H_{\text{fus}}$) 54 ± 2 kJ/mol for ZrO$_2$ and 52 ± 2 kJ/mol for HfO$_2$. They agree, within experimental uncertainties, with values from the drop and catch calorimetry from samples levitated in argon flow (Fig. 4). It must be noted, however, that calorimetry experiments performed in oxygen flow did not provide a well defined step for HfO$_2$ fusion and resulted in a larger value for ZrO$_2$ (see Supplementary Information). This cannot be related to the sample reduction during levitation in Ar flow, as the calorimeter is not enclosed in the chamber, there is enough air entering in the levitation stream through turbulence to prevent ZrO$_2$ and HfO$_2$ reduction, and the samples were white in color after the drop experiments in Ar. We attribute observed differences to possible oxygen dissolution in ZrO$_2$ and HfO$_2$ melts, an effect previously observed by Coutures in a number of oxide melts. The possibility of oxygen dissolution in molten ZrO$_2$ has profound implications for Zr-O phase equilibria at high oxygen fugacities and deserves a separate in-depth study.

In most of the assessments of the thermodynamic functions of cubic ZrO$_2$, reviewed in detail by Wang et al.33, the fusion enthalpy was kept fixed to the value 87 kJ/mol from JANAF tables14; it was optimized to 68 kJ/mol in Chen et al.’s36 assessment for the ZrO$_2$-YO$_{1.5}$ system, while Chevallier et al.34 obtained 90 kJ/mol. The value 87 kJ/mol was also accepted in the WZA6 assessment and used for the calculation of ZrO$_2$ fusion entropy ($\Delta S_{\text{fus}} = \Delta H_{\text{fus}}/T_m$ (K) = 29 [J/mol/K]). The fusion enthalpy for HfO$_2$ was then estimated6 from the melting temperature based on the assumption that it has the same fusion entropy as ZrO$_2$. It must be noted that the widely used value for $\Delta H_{\text{fus}}$ ZrO$_2$ from the JANAF Thermochemical tables14 can be traced back to the 1951 data compilation by Wagman et al.15. The same value is reported in Glushko’s35 compendium of thermodynamic properties of individual substances with reference to Kelley’s16 who calculated heats of fusions from available freezing point data of the binary systems ZrO$_2$ with SiO$_2$ and MgO. This approach is limited by a lack of information concerning activities in the liquid and solid solutions and by its reliance on the accuracy of the phase diagram determination. It is impressive that Kelley’s early assessment held for 80 years without any challenge.

| Phase/Property | Value | Method | Reference |
|----------------|-------|--------|-----------|
| Cubic ZrO$_2$  |       |        |           |
| T (T-C) trs, °C | 2311  | Experimental best value† | WZA 2006† |
| T-C, ΔV,V$_m$,%| 0.55 ± 0.09 | XRD Experiment | This work |
| Density, g/cm$^3$ | 5.61–5.53 | XRD at (2311–2710 °C) | This work |
|                | 5.54–5.44 | Ab initio MD at 2327–2727 °C | This work |
| C$_p$, J/mol/K  | 111 ± 7 | Ab initio MD at 2327–2727 °C | This work |
| Linear TEC, α, K$^{-1}$ | (1.2 ± 0.3)·10$^{-5}$ | HT XRD at (2311–2710 °C) | This work |
| Vol. TEC, α, K$^{-1}$ | (3.7 ± 0.9)·10$^{-5}$ | HT XRD at (2311–2710 °C) | This work |
|                | (4.8 ± 0.7)·10$^{-5}$ | Ab initio MD at 2527–2727 °C | This work |
| $T_{\text{vac}}$, °C | 2710 | Experimental best value† | WZA 2006† |
| $\Delta V$ on melting, % | 11 ± 2 | Ab initio MD | This work |
| $\Delta H_{\text{fus}}$, kJ/mol | 87 | Assessment | Kelley 1936† |
|                | 55 ± 7 | DnC experiment | This work |
|                | 54 ± 2 | Ab initio MD | This work |
|                | 26–49 | Classic MD | Kim et al.34 |
| $\Delta S_{\text{fus}}$, J/mol/K | 29 | Assessed $\Delta H/T_m$ (K) | WZA 2006† |
|                | 18 | Experiment $\Delta H/T_m$ (K) | This work |
|                | 17 | Ab initio MD $\Delta H/T_m$ (K) | This work |
| Liquid ZrO$_2$ |       |        |           |
| Density Liq, g/cm$^3$ | 4.86–4.74 | Ab initio MD at 2827–3127 °C | This work |
|                | 5.1–4.9 | Experiment at 2710–3000 °C | Kohara et al.11 |
| C$_p$, Liq, J/mol/K | 116 ± 25 | Ab initio MD at 2827–3127 °C | This work |
|                | 100 | Classic MD | Kim et al.34 |
| Vol. TEC, α, K$^{-1}$ | (8.7 ± 0.2)·10$^{-5}$ | Ab initio MD at 2827–3127 °C | This work |

Table 2. Thermodynamic data for cubic and liquid ZrO$_2$. †Best values for ZrO$_2$ tetragonal–cubic (T-C) transition and melting from WZA assessment of experimental results (2311 and 2710 °C) were used for temperature calibration in diffraction experiments in this work. (TEC: Thermal Expansion Coefficient, Vol.: Volumetric).

To the best of our knowledge, the volume change on melting has not been previously quantified. There are some published values for the density of liquid phases, since it has to be measured or refined for the analysis of the liquid structure by the pair distribution function (PDF) method10,11. The density of liquid ZrO$_2$ was recently measured by Kohara et al.11 from the dimensions of aerodynamically levitated liquid ZrO$_2$ spheroids. His values, 5.1–4.9 g/cm$^3$ for in 2710–3000 °C, are in good agreement with our results 4.86–4.74 g/cm$^3$ at 2827–3127 °C. The density of liquid HfO$_2$, was refined from PDF measurements by Gallington et al.10 as 8.16 g/cm$^3$, compared with 8.73–8.53 g/cm$^3$ at 2827–3127 °C from our computations.
substantially lower than Kelley’s 87 kJ/mol value included in JANAF tables 14 and used in the most current ther-
UO2, which melts at 2874 °C, there are no experimental data for the heat capacity of fluorite type oxides melting in
the 9R high temperature limit of Dulong and Petit for the contribution of lattice vibration. With the exception of
to 15R (where R is the gas constant) and substantially higher than those used in the assessments and higher than
of the Zr-O system28. In the absence of data on the thermodynamics of cubic ZrO2, they relied mostly on the
dynamic models have been proposed in recent years to model cubic zirconia and the liquid phase in assessments
values for the cubic phase when uncertainties are taken into account (see Tables 2 and 3). Five different thermo-
Δ
mol/K, which is substantially lower than
S
alent positions – cations on 4(a) at the origin and anions on 8(c) at ¼, ¼, ¼. In stoichiometric HfO2 and ZrO2,
Thermodynamic data for cubic and liquid HfO2. †Best values for HfO2 tetragonal–cubic (T-C)
Table 3. Thermodynamic data for cubic and liquid HfO2. †Best values for HfO2 tetragonal–cubic (T-C)
transition and melting from WZA 06 assessment of experimental results (2530 and 2800 °C) were used for
temperature calibration in diffraction experiments in this work. (TEC: Thermal Expansion Coefficient, Vol.: Volumetric).
The values computed for the fusion enthalpies of ZrO2 and HfO2 in this work (54 ± 2 and 52 ± 2 kJ/mol) are
substantially lower than Kelley’s 87 kJ/mol value included in JANAF tables14 and used in the most current ther-
moderamic assessments8,26. They agree, within experimental uncertainties, with our drop and catch calorimetry
measurements. Using accepted melting temperatures, the entropy of fusion for ZrO2 and HfO2 calculated as 17 J/
vol/K, which is substantially lower than ΔSfus 29 J/mol/K value obtained from Kelley’s estimate and used in the
WZA6 assessment. While our experiments were in progress, a ΔHfus for ZrO2 was reported by Kim et al.29 as
26–49 kJ/mol from classical MD simulations based on interatomic potentials. We did not locate any reports on
the computation of the fusion enthalpy of HfO2.

Heat capacities. As previously discussed37, drop and catch calorimetry cannot yet provide reasonably accu-
rate values for the heat capacity due to differences in heat loss by radiation from different temperatures. The heat
capacities of cubic ZrO2 and HfO2 obtained from ab initio MD computations are 111 ± 7 J/mol/K and 126 ± 4 J/
vol/K, respectively. The values computed for liquid ZrO2 and HfO2 at the modeled temperatures are close to the
values for the cubic phase when uncertainties are taken into account (see Tables 2 and 3). Five different thermo-
dynamic models have been proposed in recent years to model cubic zirconia and the liquid phase in assessments
of the Zr-O system29. In the absence of data on the thermodynamics of cubic ZrO2, they relied mostly on the
reproduction of ZrO2−x − Zr(O) and ZrO3−x − liquid phase boundaries37. Heat capacities of cubic and liquid ZrO2
calculated from different assessments are reviewed by Wang et al.29 and for most models, they are in the range of
75–90 J/mol/K for cubic ZrO2 and 80–100 J/mol/K for the liquid, below 3727 °C. Our computed values are close
to 15R (where R is the gas constant) and substantially higher than those used in the assessments and higher than
the 9R high temperature limit of Dulong and Petit for the contribution of lattice vibration. With the exception of
UO2, which melts at 2874 °C, there are no experimental data for the heat capacity of fluorite type oxides melting in
a comparable temperature range. Ronchi et al.26,30 reported measurements of heat capacity for UO2 from 1600 °C
to 5000 °C using a custom-designed laser flash instrumentation. Their results indicate that UO2 heat capacity
exceeds 20 R before melting, decreases to 15 R after melting and decreases further to the 9 R limit only above
4000 °C. The excess heat capacity in UO2 at high temperature is attributed to both electronic transitions and to
disorder on the oxygen sublattice. The latter is also known as the Bredig40 transition, which is common among
fluorite halides and oxides above 0.8·Tm. Clearly, the high temperature heat capacity needs further study.

Structure of cubic ZrO2 and HfO2. In the fluorite structure (Fm3m) all atoms are located on special equi-
valent positions – cations on 4(a) at the origin and anions on 8(c) at ¼, ¼, ¼. In stoichiometric HfO2 and ZrO2,
both sites are fully occupied, and the structure is uniquely defined by its unit cell parameter and the atomic dis-
placement parameters for Zr or Hf and O atoms. In ab initio MD computations, HfO2 and ZrO2 stoichiometries
were preset by the number of atoms in the simulation. High temperature diffraction experiments were performed
in oxygen flow, and the samples remained white in color after melting, but the possibility of thermally induced

| Phase/Property | Value | Method | Reference |
|----------------|-------|--------|-----------|
| Cubic HfO2     |       |        |           |
| T (T-C) trs, °C | 2530  | Experimental best value2 | WZA 20066 |
| T-C, ΔV, %     | 0.87 ± 0.08 | HT XRD Experiment³ | This work |
| Density, g/cm³ | 9.68–9.58 | XRD at (2530–2800 °C)³ | This work |
|                | 9.74–9.65 | Ab initio MD at 2527–2727 °C³ | This work |
| C_p, J/mol/K   | 126 ± 4 | Ab initio MD at 2527–2727 °C³ | This work |
| Linear TEC, α, K−1 | (1.3 ± 0.4) ·10−3 | HT XRD at (2530–2800 °C)³ | This work |
| Vol. TEC, α, K−1 | (4 ± 1) ·10−4 | HT XRD at (2311–2710 °C)³ | This work |
|                | (5.0 ± 0.7) ·10−5 | Ab initio MD at 2527–2727 °C³ | This work |
| T_melt °C      | 2800  | Experiment best value WZA 20066 | |
| ΔSfus,J/mol/K | 29    | Assessed from ZrO2 data WZA 20066 | |
|                | 20    | Experiment ΔH/T_m (K) | This work |
|                | 17    | Ab initio MD ΔH/T_m (K) | This work |
| Liquid HfO2    |       |        |           |
| Density Liq, g/cm³ | 8.73–8.53 | Ab initio MD at 2827–3127 °C | This work |
|                | 8.16  | PDF experiment Gallington 201739 | |
| C_p, J/mol/K   | 109 ± 15 | Ab initio MD at 2727–3127 °C³ | This work |
| Vol. TEC, α, K−1 | (8 ± 1) ·10−4 | Ab initio MD at 2827–3127 °C³ | This work |
oxygen defects in the cubic phases cannot be ruled out. The quality of the diffraction data did not allow refinement of oxygen occupancies due to the strong correlation with atomic displacement parameters (ADP). Isotropic ADPs were refined from selected XRD patterns as mean square displacement amplitude $U_{iso}$ (Å$^2$) and estimated from snapshots of MD trajectories (see Supplementary Information).

**Figure 2.** Center: contour plots of X-ray diffraction (XRD) patterns ($\lambda = 0.12359$ Å) with cubic ZrO$_2$ and HfO$_2$ from tetragonal-to-cubic transition to melting onset. The patterns obtained from ab initio MD simulations are included for comparison. Top and bottom: Pawley refinements of XRD patterns of cubic ZrO$_2$ and HfO$_2$ in the presence of melt and tetragonal phase (experimental data points, modeled pattern and difference curve). See Supplementary Information for refinement results for all patterns depicted in contour plots.

**Figure 3.** Density change on melting of cubic ZrO$_2$ and HfO$_2$ from ab initio MD computations with overlayed experimental results from high temperature X-ray diffraction (XRD). Uncertainties from computation and experiment are smaller than the symbol size. (The computational results are in Table 1, the results of Pawley refinement of XRD patterns are provided in Supplementary Information).
are in agreement from XRD and MD and vary within 0.03–0.05 Å² for cations and increase from 0.03 to 0.07 Å² for oxygen in hafnia. Both experiment and computation indicate larger displacement amplitudes for oxygen in zirconia: Oxygen U_{iso} was determined to range from 0.08 to 0.15 Å² from XRD data, while MD results indicate even larger amplitudes: 0.19 to 0.29 Å². It must be noted that, in our related experimental and computational study of lanthanum zirconate, we found good agreement in thermal expansion, but higher O displacement amplitudes from ab initio MD compared to those inferred from high temperature XRD data.

**Atomic diffusion in cubic and liquid ZrO_2 and HfO_2**

Diffusion rates for Zr, Hf and O in cubic phases and in the liquid obtained from simulations for cubic and liquid phases are shown in Fig. 1. The proximity of diffusion rates of oxygen in cubic and liquid phases explains high heat capacity in fluorite phase and suggests that the notion of “oxygen sublattice melting” is an accurate description of the Bredig transition. Note that tetragonal – cubic transformation in ZrO_2 and HfO_2 is suggested to be a second order transition and occurs shortly after exceeding 80% of the melting temperature threshold for the Bredig transition in fluorite structure.

Diffusion coefficients were calculated from the MD trajectories, according to equation:

$$\langle r_i^2(t)\rangle = \frac{1}{N}\sum_{i=1}^{N}[r_i(t) - r_i(0)]^2 = 6D t,$$

where D is diffusion coefficient, t is time, r is atomic position and N is number of atoms. Temperature dependent diffusion coefficients are summarized in the Supplementary Information. Our computations show negligible Zr and Hf diffusion rates in stability range of cubic phases: within 0.4–0.7·10^{-6} cm²/s for Zr and 0.1–0.3·10^{-6} cm²/s for Hf. Oxygen diffusion coefficients above tetragonal–cubic transition temperatures are an order of magnitude higher than those for cations, which suggests significant oxygen diffusion. Notably, modeling cubic HfO_2 200°C below its stability field does not show noticeable difference in Hf diffusion coefficient but show 10 fold decrease in oxygen diffusion (Table S5). Kilo et al. reported MD computations of oxygen diffusion in YSZ with 8 and 24 mol % Y₂O₃ from 400 to 1600°C. Figure 5 show oxygen diffusion coefficients in ZrO₂ as a function of temperature and in the liquid obtained from simulations for cubic and liquid phases are shown in Fig. 1. The proximity of diffusion rates of oxygen in cubic and liquid phases explains high heat capacity in fluorite phase and suggests that the notion of “oxygen sublattice melting” is an accurate description of the Bredig transition. Note that tetragonal – cubic transformation in ZrO₂ and HfO₂ is suggested to be a second order transition and occurs shortly after exceeding 80% of the melting temperature threshold for the Bredig transition in fluorite structure.

**Comparison with UO_2, ThO_2, and fluorite-related bixbyte and pyrochlore structures.**

Thoria and urania both retain a fluorite structure from ambient temperature to their respective melting points (2874 and 3367°C). Both oxides are believed to exhibit Bredig transitions above 0.8·T_{m}. ThO₂ is the only known Th oxide and expected to be more similar to cubic HfO₂ and ZrO₂ than UO₂ which is known to exhibit electronic transitions and substantial hypo- and hyperstoichiometry ranges with a fraction of U going into trivalent or pentavalent states. For UO₂ at above 0.8·T_{m} the linear thermal expansion increases to 30·10^{-6} K^{-1}, Oxygen U_{iso} to 0.12 Å², and melting is accompanied by 10 ± 1% volume increase. The data for ThO₂ at above 0.8·T_{m} are scarce, hence the thermal expansion at the melting point was extrapolated to be 14·10^{-6} K^{-1}, and Oxygen U_{iso} follows the trend for UO₂, but was not measured above 0.8·T_{m}.

YbO₂ and Lu₂O₃ melt at 2435 and 2490°C, respectively, and are stable in bixbyte or C-type structure (Ia₃, Z = 16), which is often described as a derivative of a defected fluorite structure having ordered vacancies. Their linear thermal expansion was studied both in argon and oxygen and was reported to not exceed 8.5·10^{-6} K^{-1} with U_{iso} values for Yb and Lu below 0.05 Å² up to the melting temperature and U_{iso} values for O less than 0.07 Å². Lanthanum zirconate (La₃Zr₂O₇ or LZ) is an example of compound stable up to the melting point in the pyrochlore (Fd₃m, Z = 8) structure, which is often described as a defected fluorite structure with ordering of both cations and oxygen vacancies. Neutron diffraction in Ar atmosphere indicates that it does not display an anomalous thermal expansion or oxygen mobility indicative of a Bredig transition. The linear thermal expansion of LZ was reported as ~7·10^{-6} K^{-1} from above 1650°C to the melting temperature of 2300°C, with U_{iso} values for O and La not exceeding 0.07 Å² and that of Zr remaining below 0.03 Å².

The linear thermal expansion of fluorite ZrO₂ and HfO₂ (~12·10^{-6} K^{-1}) are substantially higher than for LZ and C-type Yb₂O₃ and Lu₂O₃ (~8.5·10^{-6} K^{-1}), and lower than that observed before melting in UO₂ (~30·10^{-6} K^{-1}).
and defect fluorite YSZ (~25·10⁻⁶ K⁻¹)²⁰, and similar to the value accepted⁴⁴ for ThO₂ (14·10⁻⁶ K⁻¹). Notably, despite apparently higher oxygen mobility in ZrO₂ than in HfO₂, their molar heat capacities and volume changes on melting are the same within uncertainties. Computational and experimental results suggest dynamic disorder on the O sublattice in both ZrO₂ and HfO₂.

Conclusion

The performed computations and experiments fill gaps in the available thermodynamic data for pure ZrO₂ and HfO₂ at temperatures where the cubic fluorite phase is stable and into the liquid range, thereby facilitating future assessments. The experimental confirmation of thermal expansion and fusion enthalpies validate the accuracy of computational approaches and open the way for further computational studies of the high temperature thermodynamics of more complex systems. Our combined approaches are easy to generalize from HfO₂ and ZrO₂ to a broader range of systems. Indeed, we have applied the same combined experimental and computational methods to a wide range of oxides (e.g., Y₂O₃¹⁸, La₂Zr₂O₇⁴¹, and several rare earth oxides). In addition, the computational method has been employed to study dozens of systems⁴⁵, including oxides⁴⁶, carbides, such as the Hf-Ta-C-N system⁴⁷, and metals⁴⁸.

Methods

Computations. We employed first-principles density functional theory⁴⁹ to model HfO₂ and ZrO₂. All electronic structures were calculated by the Vienna Ab-initio Simulation Package (VASP)⁵⁰, with the projector-augmented-wave (PAW)⁵¹ implementation and the generalized gradient approximation (GGA) for exchange-correlation energy, in the form known as Perdew-Burke-Ernzerhof (PBE)⁵². The valence configuration was ([Ar]3d¹⁰)⁴s²⁴p⁶ for zirconium; for oxygen, the 2s and 2p electrons were relaxed with cutoff radius of 0.820 Å. This required a plane-wave basis set with the cutoff energy of 400 eV.

The electronic temperature was accounted for by imposing a Fermi distribution of electrons on the energy level density of states. The electronic temperature was set consistently with the ionic temperature. We used automated k-meshes generation with a k-point density of 15³/Å⁻³ in the Brillouin zone. First-principles molecular dynamics (MD) techniques were utilized to simulate atomic movements and trajectories. The MD simulations were carried out under a constant number of atoms, pressure and temperature condition (NPT, isothermal-isobaric ensemble) with a time step around 2fs. The thermostat was conducted under the Nosé-Hoover chain formalism⁵³,⁵⁴. The barostat was realized by adjusting the volume every 80 steps according to average pressure. Although this did not formally generate an isobaric ensemble, this approach has been shown⁵⁵ to provide an effective way to change volume smoothly and to avoid the unphysically large oscillation caused by commonly used barostats. MD simulations were carried out with 90 Zr (or Hf) and 180 O atoms in a periodic cell. Employing periodic boundary conditions is a completely standard way to model extended condensed phases in these types of calculations. The cell size is as large as 16 Å to reduce the finite-size effect. The liquid phase was prepared by heating the solid up to 6000 K (about twice the melting temperature) for 0.5 picoseconds. The liquid is then cooled to the simulation temperature. MD simulations were performed for a sufficiently long time to achieve convergence. The length of MD trajectory varies from 14 to 62 picoseconds, depending on convergence, but generally, 30–50 picoseconds were sufficient. On average, computations took about 25,000 CPU hours per data point, which required around two weeks on 64 cores of a computer cluster. Theoretical X-ray diffraction calculations were carried out using the AFLOW package⁴⁶. MD trajectory was sampled every 80 ionic steps, which formed a set of snapshots that were used to generate X-ray diffraction patterns averaged for the final analysis.

Experiments. X-ray diffraction (XRD) and calorimetry experiments were performed on polycrystalline ZrO₂ and HfO₂ beads, 2–3 mm in diameter, prepared by melting of powders purchased from Alfa Aesar (99.98% or higher metals purity) with a 400 W CO₂ laser. Samples were first melted into oblate spheroids in a copper

Figure 5. Oxygen diffusion coefficients in pure zirconia computed in this work compare with values for YSZ with 8% and 24% Y₂O₃ extrapolated to 2727 °C from Kilo et al.⁴¹.
hearth, followed by melting in an aerodynamic levitator, as described in detail elsewhere. High temperature XRD experiments were performed with the aerodynamic levitator at beamline 6-ID-D at the Advanced Photon Source (APS) at Argonne National Laboratory. Diffraction images were collected with a Perkin Elmer XRD1621 diffractometer. A detector was mounted 15.2 cm from the sample for transmission through the upper part of laser heated beads freely rotating in oxygen flow through a levitator nozzle. The X-ray beam (λ = 0.12359(7) Å) was collimated to 0.5 mm wide, 0.2 mm tall rectangular shape. All images were recorded as a sum of 120 0.1 s exposures. The diffraction images at room temperature with the laser off were recorded first; then the sample was heated by a 400 W CO2 laser in 50–100 °C increments as monitored with a Chino IR-CA58CS pyrometer with 1 mm spot size set to 0.92 emissivity and 0.85 window transmission corrections. Image calibration, integration, and sequential Pawley and Rietveld refinements of XRD patterns were performed with the GSAS-II software, backgrounds were fitted manually for each pattern and were not refined. NIST CeO2, SRM674b powder standard was used to calibrate detector tilt and rotation angles, beam center position and sample to detector distance (1036.2 mm). Unit cell parameters for laser melted monoclinic ZrO2 and HfO2 were refined using conventional powder XRD with internal NIST Si640C standard and Bruker D8 instrument. In a sequential refinement of high temperature patterns, sample placement was refined for each sample bead at room temperature from calibrated cell parameter and fixed for all refinements of high temperature patterns. In Rietveld refinements, sample absorption and oxygen occupancy were not refined to avoid correlation with atomic displacement parameters. Fusion enthalpies for ZrO2 and HfO2 were measured using drop and catch calorimetry. The technique and apparatus were described in detail elsewhere. Schematic diagrams and photographs are provided in Supplementary Information together with data from all experiments.

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Author Contributions
All computations were performed by Q.H. and A.v.d.W. Calorimetry experiments were performed by D.K. High temperature diffraction experiments were performed by S.U., D.K., R.W. and C.B. and data were analyzed by S.U. Each of the authors contributed to the writing and review of the manuscript.

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