# A New Polymorph of $ZrW_2O_8$ Synthesized at High Pressures and High Temperatures

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Pressure-induced amorphization of materials with negative thermal expansion is believed to arise from uncorrelated tiltings of polyhedra, kinetically frozen in an orientationally disordered state at room temperature. The transition to an amorphous phase in zircon tungstate $ZrW_2O_8$ occurs above 1.5 GPa upon cold compaction. Our synchrotron angle-dispersive X-ray powder diffraction experiments show that at high temperatures the framework structure of $ZrW_2O_8$ irreversibly collapses to a new dense hexagonal $U_3O_8$-type polymorph at pressures just after the completion of amorphization. In this structure, the Zr and W atoms are 6-fold coordinated and statistically disordered. Upon heating at higher pressures, the amorphous $ZrW_2O_8$ material decomposes into its constituent oxides. The results of our work suggest that the phenomenon underlying the pressure-induced amorphization of zircon tungstate may involve profound changes in the coordination environments of the atoms.

## Introduction

Zirconium tungstate $ZrW_2O_8$ is a prototype and model example of a compound with negative thermal expansion over a large temperature range.[1−4] It is of interest for applications requiring materials with engineered thermal properties. Its flexible framework structure at room temperature consists of $ZrO_6$ octahedra linked through oxygen atoms with $WO_4$ tetrahedra (space group $P2_13$). Above a kinetically limited order−disorder phase transition at 430 K, the structure of $ZrW_2O_8$ is disordered with one oxygen site half occupied (space group $Pa\bar{3}$).[1,5] There is no consensus on the nature of this transformation. Hashimoto et al.[6] claim the presense of two kinds of phase transitions observed at 396 and 437 K. They are supposed to be of the first- and second-order character, respectively. Nevertheless, the negative thermal expansion from 0.3 to 1050 K is dominated by rotational vibrations of the polyhedra rather than by changes in bond distances.[1−4] Zirconium tungstate is metastable at atmospheric pressure with an incongruent decomposition and narrow stability range from 1378 to 1530 K.[7] Fast quenching is required since $ZrW_2O_8$ decomposes into $ZrO_2$ and $WO_3$ below 1378 K.

At a pressure of 0.21 GPa ($T = 300$ K), the $P2_13$ phase undergoes a first-order phase transition, accompanied by a 5% reduction in volume, to an orthorhombic polymorph (space group $P2_12_12_1$), in principle maintaining the octahedral $ZrO_6$ units, but with increased average tungsten coordination numbers.[8−10] Upon further compression, $ZrW_2O_8$ irreversibly amorphizes above 1.5 GPa.[11,12] The mechanism of pressure-induced amorphization, i.e., a loss of translational or orientational long-range order, is usually discussed in terms of a thermodynamic melting, kinetic inhibition of a phase transformation to a high-pressure polymorph, dynamical lattice instability, or decomposition.[13−15] Irreversible amorphization, related to a hindrance of atomic mobility at kinetically low temperatures, is considered as due to a deformation of a crystal lattice by nucleation of a new polymorph with crystallite sizes below the coherence length of X-ray diffraction (i.e., an "X-ray diffraction" amorphous solid). In the case of zirconium tungstate, the amorphization under pressure has been interpreted as involving unconcerted rotations of the polyhedra, kinetically trapped in an orientationally disordered

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state.[11] It has been concluded that the behavior of zirconium tungstate illustrates a general correlation between negative thermal expansion and pressure-induced amorphization in highly flexible framework structures.

The work reported here examines the high-pressure behavior of $ZrW_2O_8$ with the aim to elucidate the mechanism of kinetically inhibited equilibrium processes in this material at room temperature and eventually to search for new polymorphs by carrying out synchrotron angle-dispersive X-ray powder diffraction simultaneously at high pressures and high temperatures. We observe a complete breakdown of the framework structure of $ZrW_2O_8$ resulting in a transformation to an as yet unknown crystalline modification at pressures just after the completion of amorphization and a decomposition to denser components at higher pressures. The new structure is of the α-$U_3O_8$ type (space group $P\bar{6}2m$) with Zr and W atoms 6-fold coordinated and statistically disordered. The hexagonal phase is found to be stable to at least 1100 K at ambient pressures, i.e., to above the decomposition temperature of framework $ZrW_2O_8$ at 1 atm.[7]

## Experimental Section

The sample of $ZrW_2O_8$ was prepared by a ceramic method from a stoichiometric mixture of zirconium and tungsten oxides rapidly quenched to room temperature from 1473 K.[11,12] The final product contained less than 3% of $WO_3$ as an impurity. The angle-dispersive X-ray powder diffraction experiments at high pressures and high temperatures [$\lambda = 0.26473(1)$ Å] were carried out using the large-volume Paris-Edinburgh facility at the ID30 beamline of the European Synchrotron Radiation Facility, Grenoble, France.[16] A recently developed multislit system was employed during the experiment, which allows sample diffraction patterns to be taken with a minimum of signal from the capsule, surrounding furnace, and B-epoxy gasket (see Supporting Information). Pressure was determined from the lattice parameters of the h-BN capsule material which were measured in separate scans.[17] Temperature was determined from furnace power curves that have been calibrated by known fusion curves and an internal cross-calibration method.[18] Representative errors in pressures are 0.1 GPa. The relative errors in temperatures do not exceed 10%. X-ray powder patterns of samples recovered to ambient conditions, containing traces of the sample assembly (h-BN and graphite), were measured at the same beamline with a wavelength $\lambda = 0.3738(1)$ Å. Differential scanning calorimetry (DSC) experiments were performed in the 373−1100 K temperature range with a heating rate of 40 K/min under argon atmosphere ($P$ = 1 atm).

## Results and Discussion

The first series of measurements was carried out in situ upon heating at 5−5.5 GPa (Figure 1a) Up to about 1000 K, the patterns are typical of the amorphous phase and diffraction peaks cannot be distinguished from the background. At higher temperatures, well separated and sharp peaks due to a crystalline material appear.

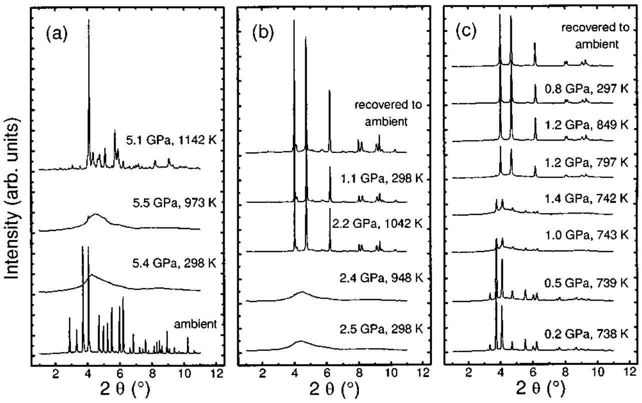

**Figure 1.** Selected X-ray diffraction patterns of $ZrW_2O_8$ at different conditions ($\lambda = 0.26473$ Å). The pattern at ambient pressure in part a is due to the $P2_13$ phase of $ZrW_2O_8$. The sample turns amorphous during compression to 5.4 GPa. Diagrams in part b refer to heating after precompression to a lower pressure of 2.5 GPa. A new polymorph of $ZrW_2O_8$ is formed near 1000 ± 50 K which can be recovered to ambient conditions. Patterns in part c demonstrate that the same polymorph can be obtained from the $Pa\bar{3}$ phase on compressing and heating to 1.4 GPa and 742 K.

In an additional set of experiments we studied the high-pressure and high-temperature behavior of pure $WO_3$ and $ZrO_2$ oxides that are the simplest decomposition products of $ZrW_2O_8$ to exclude any possibility of a chemical reaction between the oxides and sample assembly material. Indeed, we do not observe any chemical reactions. Accordingly, the pattern collected at 5.1 GPa and 1142 K demonstrates that $ZrW_2O_8$ is decomposed into the component $ZrO_2$, $WO_3$, and other mixed Zr−W oxides as inferred from the comparison of these new X-ray patterns with the ones for $ZrO_2$ and $WO_3$. Selected results are given in the Supporting Information; however, their detailed analysis is beyond the scope of the present paper.

When the sample is heated at 2.2−2.5 GPa, just after the pressure-induced amorphization has been completed, the observed diagrams evolve in a different way (Figure 1b). Up to about 1000 K, the patterns are again indicative of the amorphous phase. At higher temperatures a new crystalline phase occurs whose patterns correspond neither to any of the features observed for $WO_3$ and $ZrO_2$ nor to the calculated diagrams assuming the known structures of related compounds like tungstates, molybdates, rhenates, etc. (refs 19−22 and references therein). This material is quenchable to ambient conditions.

We also carried out several series of measurements at which the $Pa\bar{3}$ polymorph was compressed at constant high temperature. Figure 1c presents the diagrams initially collected at about 740 K. The onset of pressure-induced amorphization is already observed at 1.0 GPa when the diffraction peaks become broad and loose their intensities. When the sample is heated only by about 50 K at 1.4 GPa, a new phase appears with an X-ray

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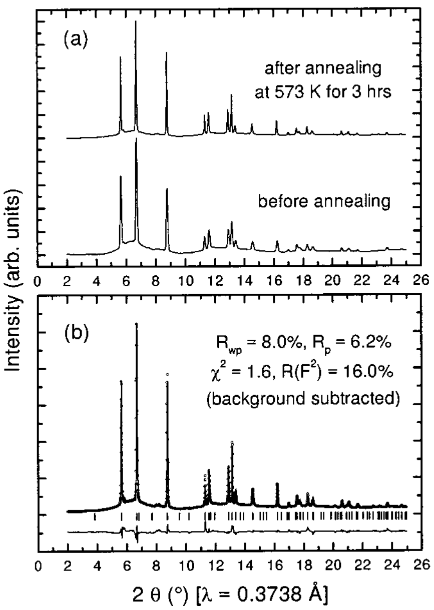

**Figure 2.** X-ray diffraction patterns of the $ZrW_2O_8$ sample recovered to ambient pressure and room temperature from 2.2 GPa and 1042 K. The patterns before and after annealing in the air at 573 K for 3 h ($P = 1$ atm) are shown in part a. Part b shows the result of a full Rietveld refinement of the X-ray powder pattern for the annealed $ZrW_2O_8$ sample based on a cation-disordered α-$U_3O_8$-type structure: $P\bar{6}2m$, $Z = 1$, $a = 6.4158(2)$ Å, and $c = 3.7940(1)$ Å. The open symbols represent experimental data, and the line running through the data refers to the calculated pattern. The corresponding difference curve is plotted below the observed and calculated diagrams. The tick marks indicate the calculated Bragg reflections.

diagram very similar to the one previously observed at 2.2 GPa and 1042 K (Figure 1b). The pattern at 1.2 GPa and 797 K (Figure 1c) also contains traces of the partially amorphized $Pa\bar{3}$ polymorph of $ZrW_2O_8$. The $Pa\bar{3}$ polymorph completely disappears at higher temperatures, and the new phase is again quenched to ambient conditions. Our experiments at different pressure−temperature conditions indicate that the pressure at which the onset of amorphization takes place decreases with increasing temperature both for the $P2_12_12_1$ and $Pa\bar{3}$ polymorphs. It is noteworthy that the $Pa\bar{3}$ phase is still present above 1.2 GPa at 800 K, while at room temperature the $P2_13$ modification already transforms into the $P2_12_12_1$ polymorph at 0.21 GPa. This observation, suggesting a limited pressure−temperature occurrence field of the $P2_13$ phase, warrants a detailed investigation of the phase diagram of this material.

The dark gray product (due to traces of graphite) recovered from 2.2 GPa and 1042 K was further studied at atmospheric pressure. The initial X-ray pattern contains slightly broadened peaks with relatively high background due to partially amorphous components (Figure 2a). After annealing this sample for a prolonged time in the air at 573 K, the amorphous background is largely diminished while the peaks become sharper. There was no color change after the annealing. The differential scanning calorimetry experiments on the same sample and the analysis of its X-ray powder pattern after the DSC heating−cooling cycle indicate that this new phase is stable to at least 1100 K, i.e., to above the decomposition temperature of framework $ZrW_2O_8$ at ambient pressure.[7]

The pattern of the sample annealed at 573 K, excluding the traces of the sample assembly and initial $WO_3$ impurity, can be indexed[23] on the basis of a hexagonal unit cell with $a = 6.4145(3)$ Å, $c = 3.7941(2)$ Å, and $V = 135.20$ Å$^3$ with no extinction rules [M(19) = 97.7, F(19) = 244.9 (0.0017, 46)]. The volume of 135.20 Å$^3$ is 42% and 35% smaller than the volumes for one formula unit in the $P2_13$ ($Z = 4$) [1] and $P2_12_12_1$ ($Z = 12$) [8] polymorphs, respectively. Such dramatic volume reduction could be explained by massive structural transformations leading to a more efficient packing of the atoms. The only known $AB_2X_8$-type structure with similar lattice parameters is the structure of $UTa_2O_8$ ($P\bar{3}1m$, $Z = 1$).[24] However, the calculated intensities after replacing the U and Ta atoms by Zr and W, respectively, are completely different from the observed ones. Then, we applied different techniques to solve this new structure using direct, heavy atom, and global optimization methods with the assumption that the $Z$ parameter is equal to 1 and the hexagonal/trigonal space group would be one of the space groups for which the extinction symbol is $P$- - -. In all cases, the obtained site multiplicities for Zr and W did not give the required 1:2 ratio if the ordered cations are to occupy separate sites and the Zr−W distances were unacceptably short. This observation suggests that the Zr and W atoms in the new structure of zirconium tungstate could in fact be disordered.

A search for possible related materials, whose structures would imply the Zr/W cation disorder in the hexagonal/trigonal lattice with $a = 6.415$ Å and $c = 3.794$ Å, yields α-$U_3O_8$ ($P\bar{6}2m$, $Z = 1$)[25−27]at which the U atoms occupy one 3$f$ site, while the oxygen atoms reside at the sites 2$c$, 3$g$, and 3$f$. In this structure, the cations are in chains of vertex-sharing pentagonal bipyramids (Figure 3). There is good agreement between the observed pattern of the annealed $ZrW_2O_8$ sample and the calculated one assuming the hexagonal $U_3O_8$ structural model with the U atoms replaced by Zr and W atoms with occupancies equal to $^1/_3$ and $^2/_3$, respectively, and with all the positional parameters for the cations and oxygen atoms fixed to the values given by Loopstra:[25] Zr and W at (0.3526,0,0), oxygens at ($^1/_3$,$^2/_3$,0), (0.3609,0,$^1/_2$), and (0.7453,0,0). Adopting this structure implies that the Zr and W atoms are statistically disordered at the same crystallographic site of the high-pressure high-temperature modification of $ZrW_2O_8$.

The results of a corresponding full profile Rietveld refinement[28] are given in Figure 2b and Table 1. The starting atomic parameters used in the refinement were the ones given for α-$U_3O_8$. The refined parameters were: the fractional coordinates of the atoms, isotropic thermal parameters, Chebyshev polynomial background, Stephens profile function, an overall intensity scaling factor, and cell parameters. The (Zr,W)−O(1) distances are 2.85(6) Å and (2×) 1.91(1) Å, (Zr,W)−O(2) are (2×) 1.905(3) Å, and (Zr,W)−O(3) are (2×) 2.119(2) Å. For

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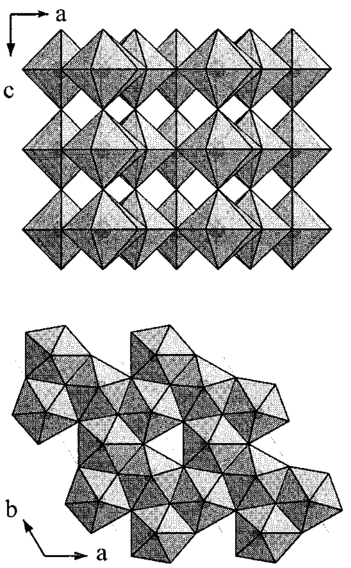

**Figure 3.** Polyhedral representation of the $U_3O_8$-type crystal structure ($P\bar{6}2m$, $Z = 1$) viewed along the *b* (top) and *c* (bottom) axes. The cations are in chains of vertex-sharing pentagonal bipyramids with the equatorial O(1) and O(3) atoms and apical O(2) atoms.

**Table 1. Structural Data Obtained from a Full Rietveld Refinement of the X-ray Powder Diffraction Pattern for the New $ZrW_2O_8$ Phase Recovered to Ambient Conditions after Synthesis at 1042 K and 2.2 GPa**[a]

| atom | site | *x* | *y* | *z* | occupancy | $U_i/U_e \times 100$ |
|---|---|---|---|---|---|---|
| Zr | 3*f* | 0.3394(8) | 0.0 | 0.0 | $^1/_3$ | 3.18(2) |
| W | 3*f* | 0.3394(8) | 0.0 | 0.0 | $^2/_3$ | 3.18(2) |
| O(1) | 3*f* | 0.784(9) | 0.0 | 0.0 | 1.0 | 14.2(22) |
| O(2) | 3*g* | 0.367(4) | 0.0 | $^1/_2$ | 1.0 | 5.6(5) |
| O(3) | 2*c* | $^1/_3$ | $^2/_3$ | 0.0 | 1.0 | 2.0(4) |

[a] The pattern was collected after annealing the sample in the air at 573 K for 3 h ($P = 1$ atm). The structure is of the α-$U_3O_8$ type: space group $P\bar{6}2m$, $Z = 1$, lattice parameters $a = 6.4158(2)$ Å, $c = 3.7940(1)$ Å. The estimated standard deviations are given in brackets.

comparison, the average Zr–O and W–O distances in the ambient-pressure room-temperature structure of $ZrW_2O_8$ ($P2_13$, $Z = 4$) are 2.08 Å (octahedral coordination of Zr) and 1.76 Å (tetrahedral coordination of W), respectively.[1,2] The coordination number of the Zr and W cations, determined by the analysis of bond lengths, is six with one additional distant oxygen atom (6 + 1). Neither the patterns of the new phase collected in situ at high pressures and high temperatures nor its patterns measured at ambient conditions before and after annealing show any peak splittings or anomalous anisotropic broadening that would suggest lower symmetry of the structure, i.e., possible ordering of the Zr and W cations in the lattice, in a fashion similar to the temperature effects in the orthorhombic and hexagonal phases of $U_3O_8$.[25–27]

In the pressure region studied here, the coordination number for the W atoms in $WO_3$ is six,[29] while the coordination number for the Zr atoms in $ZrO_2$ is seven.[30] Hence, from the crystal chemistry point of view the driving force for the breakdown of framework $ZrW_2O_8$ is the instability of the tetrahedral coordination around the W atoms. In fact, the cubic-to-orthorhombic phase transition in $ZrW_2O_8$ ($P2_13 \rightarrow P2_12_12_1$) upon cold compaction at 0.21 GPa already involves the increase of the average tungsten coordination number.[8–10] Comparing the pressure dependencies of volumes in $ZrW_2O_8$ ($P2_12_12_1$, $Z = 12$) and of volumes taken by the $ZrO_2 + 2WO_3$ composite, all per one formula unit at room temperature (Figure 4), reveals that $ZrW_2O_8$ is not stable with regard to the constituent $ZrO_2$ and $WO_3$ oxides at all pressures, not just at 1 atm.[7] Up to about 4.5 GPa, the stable phase seems to be the one of the α-$U_3O_8$ type ($P\bar{6}2m$, $Z = 1$), because adopting this structure yields the smallest specific volumes.

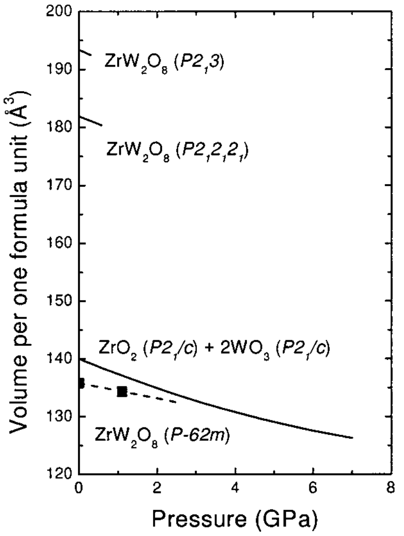

**Figure 4.** Volume as a function of pressure for $ZrW_2O_8$ and for a $ZrO_2 + 2WO_3$ composite, all at 300 K. The squares represent the room-temperature unit-cell volumes of the new phase of $ZrW_2O_8$ with the α-$U_3O_8$ structure ($P\bar{6}2m$, $Z = 1$) upon decompression after synthesis at 2.2 GPa and 1042 K. The volume (per formula unit) of this phase is 35% smaller than that of $ZrW_2O_8$ with the $P2_12_12_1$ structure. Pressure–volume data represented by solid lines are taken from the literature: ref 8 for $ZrW_2O_8$ ($P2_13$, $Z = 4$) and $ZrW_2O_8$ ($P2_12_12_1$, $Z = 12$), ref 29 for $WO_3$ ($P2_1/c$, $Z = 4$), and ref 30 for $ZrO_2$ ($P2_1/c$, $Z = 4$). The dashed line represents the tentative compression behavior of the α-$U_3O_8$-type modification at room temperature.

A brief review of phase transformations in $ZrW_2O_8$ and $ZrMo_2O_8$ could be elucidating. When compressed hydrostatically, γ-$ZrMo_2O_8$ ($Pa\bar{3}$), with the high-temperature structure of $ZrW_2O_8$, transforms above 0.7 GPa[22] to an undetermined monoclinic phase (the $\phi$ phase) that is not related to β-$ZrMo_2O_8$ ($C2/c$), a thermodynamically stable polymorph at ambient pressure and room temperature.[31] β-$ZrMo_2O_8$ has a structure with infinite ribbons of edge-sharing $ZrO_8$ polyhedra and $MoO_5$ tetragonal pyramids (or highly distorted $MoO_6$ octahedra).[31] Under nonhydrostatic conditions, cubic $ZrMo_2O_8$ amorphizes above 0.3 GPa and is transformed into the $\phi$ phase during heating at high pressures.[22] α-$ZrMo_2O_8$ ($P\bar{3}1c$), with a two-dimensional structure at which layers built of $ZrO_6$ octahedra are linked together by $MoO_4$ tetrahedra, undergoes a transformation to its distorted δ derivative ($C2/m$) at 1.1 GPa. Upon further compression, the $C2/m$ polymorph converts into a new ϵ triclinic modification ($P1$ or $P\bar{1}$).[20,21]

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The changes in specific volumes relative to the volume per one formula unit in metastable $\gamma$-$ZrMo_2O_8$ for α, $\beta$, $\delta$, $\epsilon$, and $\phi$ polymorphs are −8%, −35%, −16% (extrapolated to 0.0001 GPa), −26% (extrapolated to 0.0001 GPa), and −11% (between 0.7 and 2.0 GPa), respectively.[22,32] It is worth noticing that the largest change in specific unit cell volumes between the cubic and other $ZrMo_2O_8$ polymorphs involves the thermodynamically stable $\beta$ phase at atmospheric pressure, i.e., the polymorph without tetrahedrally coordinated Mo atoms. In the case of $ZrW_2O_8$, the cubic form ($P2_13$) transforms into the orthorhombic phase ($P2_12_12_1$) at 0.21 GPa.[8−10] The pressure-induced amorphization of this material occurs under both hydrostatic and nonhydrostatic conditions.[11,12] The results of this study show that the new high-pressure phases nucleating from the amorphous product upon heating at high pressures is hexagonal $ZrW_2O_8$ or mixed $ZrO_2$ and $WO_3$ oxides. The volume of the hexagonal phase ($P\bar{6}2m$) is 42% and 35% smaller than the volumes for one formula unit in the $P2_13$ ($Z = 4$) [1] and $P2_12_12_1$ ($Z = 12$) [8] polymorphs, respectively. Hence, further studies on the pressure−temperature phase diagram of $ZrW_2O_8$ would then deliver more information on the kinetic or thermodynamic stability of the $P\bar{6}2m$ polymorph (and its possible ordered derivatives) in respect to other $ZrW_2O_8$ modifications as well as $ZrO_2$ and $WO_3$ oxides.

## Conclusions

The amorphization of zircon tungstate $ZrW_2O_8$ upon cold compaction above 1.5 GPa has previously been interpreted as due to uncorrelated tiltings of polyhedral units that are kinetically frozen in an orientationally disordered state.[11] The present X-ray diffraction data do not provide any direct evidence on the nature of the pressure-induced amorphous phase (coordination numbers of the cations, etc.) so that investigations at high pressures and high temperatures utilizing “local probe” techniques to study the zirconium and tungstate environments are required, e.g., extended X-ray absorption fine structure (EXAFS).[19] On the other hand, at nearly room temperature, the product is amorphous because of insufficient energy to form a new crystalline phase. Our X-ray diffraction data demonstrate that, depending on the pressure at which the amorphous phase is heated, either the component oxides or a new crystalline polymorph are directly obtained. $ZrW_2O_8$ decomposes when the X-ray amorphous phase is heated in situ at pressures much higher than that for the onset of amorphization. At lower pressures just after the completion of the amorphization, a polymorph of the α-$U_3O_8$ type is obtained whose dense-packed structure does not bear any resemblance to the structure of any other known modifications: the Zr and W atoms are 6-fold coordinated with an additional distant oxygen atom (the coordination 6 + 1) and are statistically disordered in the lattice. On the basis of the observed crystalline phases nucleating from the amorphous phase, it could be suggested that there is not necessarily a connection between negative thermal expansion and pressure-induced amorphization of $ZrW_2O_8$, involving concerted and unconcerted tiltings of rigid polyhedral units, respectively, around the Zr and W atoms.[11] The results of our work rather indicate that even at room temperature the phenomenon underlying the pressure-induced amorphization of zircon tungstate may involve pronounced changes in the coordination environments of the atoms.

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**Supporting Information Available:** Figures showing the sample assembly, XRD patterns for $ZrO_2$ and $WO_3$ and XRD profiles for $ZrO_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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