# Further Contraction of ZrW$_2$O$_8$
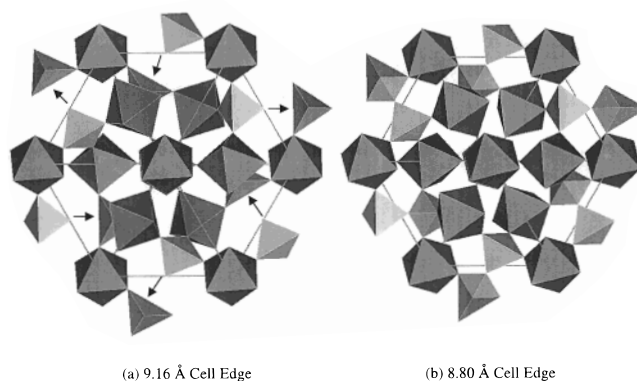
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Insertion of water into the framework of cubic ZrW$_2$O$_8$ is found to result in a volume contraction of 10% without shortening of Zr−O or W−O bond lengths. The contraction is related to twisting motions of the WO$_4$ tetrahedra and ZrO$_6$ octahedra, which are linked by corner sharing (Figure 1). Presumably, hydrogen bonding forces are responsible for pulling in the framework. Neutron diffraction data obtained on ZrW$_2$O$_8$ at 1443 K show that its unusual negative thermal expansion has continued from 1050 K at about the same magnitude as below 1050 K. Analysis of these data shows that some interatomic distances are increasing with increasing temperature as the overall structure is contracting. This suggests a contribution to negative thermal expansion not previously considered.

Zirconium tungstate, ZrW$_2$O$_8$, is apparently thermodynamically stable only from about 1380 to 1530 K.[1] It can, however, be quenched from high temperature to room temperature. It is then kinetically stable to about 1050 K. A negative thermal expansion coefficient ($\Delta l/l$) for ZrW$_2$O$_8$ has been reported from 0.3 to 1050 K.[2,3] The magnitude of this coefficient is large at room temperature, being $-9.1 \times 10^{-6}$ K$^{-1}$ for ZrW$_2$O$_8$ compared to $+6.5 \times 10^{-6}$ K$^{-1}$ for $\alpha$-Al$_2$O$_3$. This behavior for ZrW$_2$O$_8$ is especially remarkable and useful considering its cubic crystal structure. This thermal contraction has been attributed to transverse vibrational modes of O in Zr−O−W linkages.[2−4] Heat capacity measurements, inelastic neutron scattering experiments, and analysis of the thermal expansion data have provided experimental evidence for these low-energy modes.[5−7] No structural information on ZrW$_2$O$_8$ has been previously reported in the temperature range where it is thermodynamically stable.

Neutron diffraction data[8] obtained at 1443 K show that the negative thermal expansion of ZrW$_2$O$_8$ continues up to this temperature (Figure 2). Above a phase transition at 428 K, the pair of WO$_4$ tetrahedra may be considered to have merged into a W$_2$O$_8$ group with a bridging oxygen (Figure 3).[3] The O3 position is 50% occupied, and ZrW$_2$O$_8$ has been shown to possess high

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(8) A ZrW$_2$O$_8$ pellet 0.5 in. in diameter and 1 in. in length was suspended with Pt wire in a furnace on the BT-1 high-resolution diffractometer at the NIST reactor. A Cu(311) monochromator with a 90° takeoff angle, $\theta = 1.5402$ Å, and in-pile collimation of 15 ft were used to collect data from 3 to 168° $2\theta$ with a step size of 0.05°. The sample was heated as rapidly as possible to 1403 K. A neutron diffraction pattern obtained at this temperature indicated that ZrW$_2$O$_8$ had largely decomposed into ZrO$_2$ and WO$_3$. The temperature was raised to 1443 K, and another diffraction pattern was obtained which showed a strong diffraction pattern of cubic ZrW$_2$O$_8$ with a cell edge of 9.102 Å. Refinement of these data by the Rietveld method using GSAS software in space group $Pa\overline{3}$ yielded final agreement factors of $xR_p = 6.18\%$ and $R_p = 5.11\%$. Final refined positional parameters with Zr at 0, 0, 0 and O2 at 1/2, 1/2, 1/2 were $x$(W) = 0.363(1), $x$(O1) = 0.4403(8), $y$(O1) = 0.2079(6), $z$(O1) = 0.4309(8), and $x$(O3) = 0.223(1).



(a) 9.16 Å Cell Edge          (b) 8.80 Å Cell Edge

**Figure 1.** Expanded (a) and contracted (b) structures of ZrW$_2$O$_8$ shown as WO$_4$ tetrahedra and ZrO$_6$ octahedra. A slight twisting of the ZrO$_6$ octahedra causes the unit cell contraction.
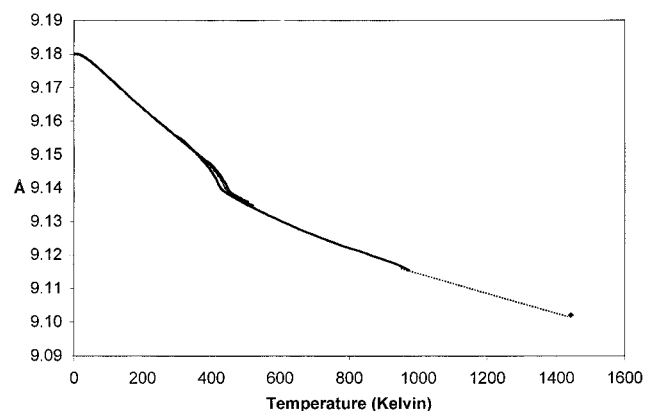


**Figure 2.** Unit cell edge of cubic ZrW$_2$O$_8$ vs temperature. The broken line connects the low-temperature data to a single point at 1443 K.
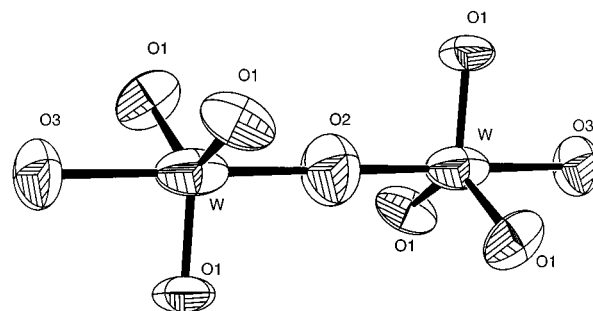


**Figure 3.** Part of the ZrW$_2$O$_8$ structure where the bonds between W, O2, and O3 define the 3-fold axis. The O2 atom is on an inversion center. The O1 atoms are corners of ZrO$_6$ octahedra.

oxygen mobility.[3] Thus, this portion on the 3-fold axis is a mixture of O3−W−O2−W and W−O2−W−O3 configurations, and to a lesser extent O3−W−O2−W−O3 and W−O2−W configurations. Although the thermal ellipsoids in Figure 3 all have the shapes expected for normal thermal motion, these ellipsoids reflect in part the different atomic positions for the different configurations. With increasing temperature, there is a significant expansion of W−O bond lengths along the 3-fold axis. Distances at 483 and 1443 K are respectively 2.090 and 2.157 Å for W−O2 and 2.148 and 2.215 Å for W−O3. There is, on the other hand, a considerable shortening for the apparent W−O1 distance of 1.778 to 1.694 Å on going from 483 to 1443 K. This decrease will directly contribute to the negative thermal expansion of ZrW$_2$O$_8$, whereas the increasing W−O2 and W−O3 distances have no impact on the thermal expansion of ZrW$_2$O$_8$. The apparent

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decrease in the W−O distance may be largely due to the transverse thermal motion of O in the Zr−O−W linkages, as we and others have previously suggested.[2−7] In $Y_2W_3O_{12}$ which also shows strong negative thermal expansion, we found a decrease for the apparent W−O distance of 1.775 to 1.72 Å from 15 to 1373 K, which was attributed to transverse thermal motion in Y−O−W linkages.[9] The apparent W−O1 distance found for $ZrW_2O_8$ at 1443 K is significantly shorter than that found in $Y_2W_3O_{12}$ at 1373 K. This suggests that an additional factor is important in the negative thermal expansion of $ZrW_2O_8$. The weakening of the W−O2 and W−O3 bonds with increasing temperature causes the W−O1 bonds to become stronger and shorter.

Hydration of $ZrW_2O_8$ is not observed at room temperature or at 100 °C under water. However, we find that exposing $ZrW_2O_8$ to water at higher temperature can cause insertion of water into this open framework structure up to 1 mol of water for 1 mol of $ZrW_2O_8$.[10] This water insertion causes a dramatic decrease in the unit cell size of $ZrW_2O_8$ (Figure 4) demonstrating that the $ZrW_2O_8$ framework can shrink much more than occurs by thermal contraction up to 1443 K. Assuming the thermal expansion coefficient of $-3.9 \times 10^{-6}$ K$^{-1}$ observed for $ZrW_2O_8$ from 483 to 1443 K, a temperature of over 8000 K would be required for thermal contraction to equal the impact of inserted water. Given the compressibility of $1.44 \times 10^{-3}$ kbar$^{-1}$ measured[11] for $ZrW_2O_8$, a pressure of about 700 kbar would be required to equal the compressive effect of inserted water. Once the water has been inserted into $ZrW_2O_8$, its thermal expansion becomes weakly positive.[12] We conclude that the inserted water pulls in the structure through hydrogen bonding. The water within the

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(10) A typical experiment was based on heating 1 g of $ZrW_2O_8$ in a 40 mL Parr bomb with 15 mL of water for 24 h at 180 °C. Water content of the product was determined by thermogravimetric analysis.

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(12) From 15 to 298 K, thermal expansion coefficients of +1.9 and +2.0 $\times$ 10$^{-6}$ K$^{-1}$ were found for $ZrW_2O_8 \cdot 0.55H_2O$ and $ZrW_2O_8 \cdot 0.75H_2O$, respectively.

(13) Rietveld refinements were conducted on three partially hydrated samples using data collected at both 15 and 298 K. These refinements confirm that the framework has remained intact, that the space group is *Pa*3, and that the Zr−O−W angle has decreased by about 3° in a 55% hydrated sample. Exact placement of the inserted water was precluded by the several types of disorder present: the partial occupancy of the water and orientational disorder for both water and the $WO_4$ tetrahedra.
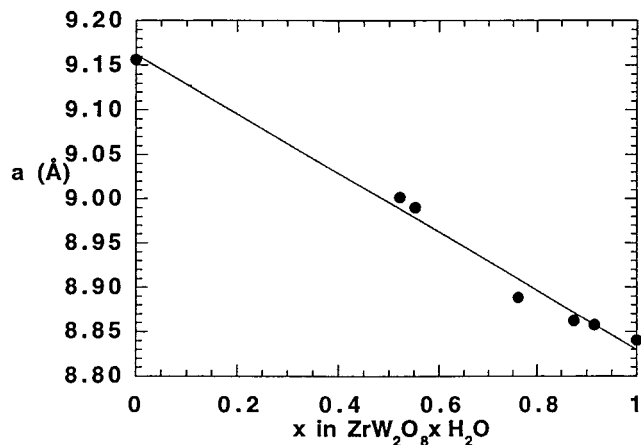


**Figure 4.** The 298 K unit cell edge of $ZrW_2O_8$ on hydration.

framework disrupts the dynamic rocking motions of the $WO_4$ tetrahedra and $ZrO_6$ octahedra which are primarily responsible for the thermal contraction of $ZrW_2O_8$. The hydration reactions are readily reversible with anhydrous cubic $ZrW_2O_8$ being reformed on heating the hydrated samples to 423 K in air. Considering the conditions required for hydration of $ZrW_2O_8$, this hydration reaction will not likely be a problem for applications of $ZrW_2O_8$. However, we have observed that in samples with Mo substituted for W this hydration reaction occurs slowly in air at room temperature.

The basic framework formula for $ZrW_2O_8$ is $ZrW_2O_6$ where all framework oxygen is shared between one Zr and one W atom. The additional nonframework oxygen atoms are bound to W only. Any dimensional change in the framework must be reflected in framework bond distances or in the Zr−O−W angle. Variation in the Zr−O−W angle is not a significant factor in the thermal contraction of $ZrW_2O_8$. However, the framework collapse caused by the water insertion has occurred with a significant decrease in the Zr−O−W angle and thus also in the Zr−W distance.[13]