



	Experiment title: X-ray diffraction study of ZrW_2O_8 at high pressures and high temperatures	Experiment number: CH982
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Report:

ZrW_2O_8 is a prototype and model example of a compound with a negative thermal expansion over a large temperature range for applications in materials with engineered thermal properties [1,2]. Its very flexible structure at room temperature consists of ZrO_6 octahedra linked through oxygen atoms with WO_4 tetrahedra ($P2_13$). Above the second-order phase transition at 428 K, the structure of ZrW_2O_8 is disordered with one oxygen site half occupied ($Pa\bar{3}$). The negative thermal expansion from 0.3 K to 1050 K, i.e., to the decomposition temperature, is dominated by rotational motions of the polyhedra rather than by changes in bond distances. At high pressures and room temperature, the $P2_13$ phase undergoes a first-order phase transition to an orthorhombic polymorph at 0.21 GPa ($P2_12_12_1$) [3]. Upon further compression, ZrW_2O_8 irreversibly amorphizes in the range 1.5-3.5 GPa [4]. The mechanism of pressure induced amorphization in this material has been described as involving uncorrelated tiltings of the polyhedra, kinetically frozen in an orientationally disordered state, with a possibility of changes in cation coordination.

The irreversible pressure-induced amorphization is commonly attributed to the nucleation of a high-pressure phase from the parent polymorph but thermal energy is not kinetically high enough to produce large crystallite size coherent to x-ray radiation. At low temperatures, atomic mobility and crystallite growth are hindered. However, larger crystallites are grown at higher temperatures. The amorphous phase without its strict P - T stability fields cannot be defined as a thermodynamically stable phase but as a state in a kinetic process.

We carried out several series of measurements at different pressure-temperature conditions using *in situ* angle-dispersive synchrotron x-ray powder diffraction in a large volume Paris-Edinburgh cell (to be submitted). The results of our study show that the pressure-induced phenomena in highly flexible framework of ZrW_2O_8 are more complicated. This material indeed amorphizes above 1.5 GPa at room temperature. However, depending on the pressure at which the sample is heated, either the *component oxides* or a *new crystalline polymorph* are obtained. This shows that the metastable amorphization is not necessarily a precursor phenomenon to a kinetically hindered phase transition, only. Indeed, 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, a structure solution of the new phase shows that it is of the α - U_3O_8 type with a dense-packed structure with no resemblance to the framework of any other known polymorphs of related tungstates, molybdates, rhenates, etc.: the Zr and W atoms are six-fold coordinated (with an additional distant oxygen atom) and are statistically disordered in the lattice. Moreover, 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.

In the structure of $\alpha\text{-U}_3\text{O}_8$ ($P\bar{6}2m$, $Z = 1$), the U atoms occupy one $3f$ site, while the oxygen atoms reside at the sites $2c$, $3g$, and $3f$ [5]. The U atom is bonded to six oxygens at distances between 2.07 Å and 2.26 Å, with an additional oxygen atom located at 2.55 Å, i.e., the U atoms are in chains of vertex-sharing pentagonal bipyramids. There is excellent agreement between the observed pattern of the new phase 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 [5] for $\alpha\text{-U}_3\text{O}_8$ (Figure 1). Adopting this structure implies that the Zr and W atoms are statistically disordered at the same crystallographic site of the high-pressure high-temperature structure of ZrW_2O_8 . The coordination number of the cations, determined by the analysis of bond lengths, is six with one additional distant oxygen atom. The packing of the atoms in this structure is more efficient than that in the highly flexible frameworks found in the $P2_13$, $Pa\bar{3}$, and $P2_12_12_1$ phases as, for instance, inferred from the comparison of the unit cell volumes - the unit cell volume of 135.21 Å³ in the $P\bar{6}2m$ ($Z = 1$) phase is 42% and 35% smaller than the volumes for one formula unit in the $P2_13$ and $P2_12_12_1$ polymorphs, respectively. It should be added that 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 similar fashion to the temperature effects in the orthorhombic and hexagonal phases of U_3O_8 .

Our observations show that there occur two competing kinetically constrained pressure-induced processes in zirconium tungstate as a result of a complete collapse of the mixed tetrahedral-octahedral framework: a structural transformation to another crystalline phase and a decomposition to denser components. In both cases, the initial size of crystallites at room temperature is below the coherence length for x-ray diffraction. It should be recalled that in the pressure region studied here, the coordination number for the W atoms in WO_3 is 6, while the coordination number for the Zr atoms in ZrO_2 is 7. Hence, from the crystal chemistry point of view, the driving force for the break-down of framework ZrW_2O_8 is the pressure instability of the tetrahedral coordination around the W atoms leading to the formation of the $\alpha\text{-U}_3\text{O}_8$ -type phase at pressures just after the amorphization has been completed or to the decomposition into component ZrO_2 and WO_3 oxides at higher pressures.

We expect that an intimate interplay between the two competing processes in several other highly flexible framework compounds at high pressures and high temperatures would lead to synthesis of novel materials.

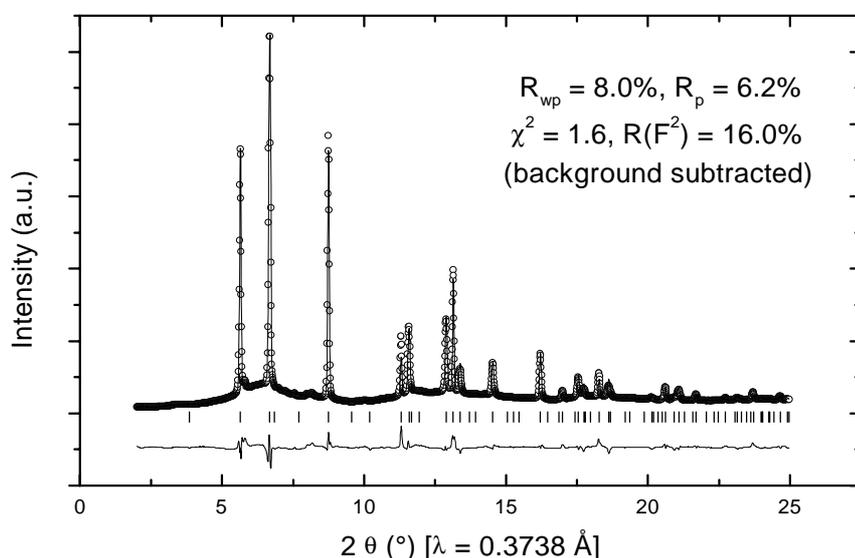


Figure 1 Observed, calculated, and difference XRD profiles of the ZrW_2O_8 sample recovered to ambient conditions: the $\alpha\text{-U}_3\text{O}_8$ -type structure. Vertical markers indicate Bragg reflections.

References

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