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New polymorph of $HfMo_2O_8$ synthesized using a high-pressure and high-temperature toroid anvil setup

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We report the synthesis and characterization of a new polymorph (β) of $HfMo_2O_8$. This phase is synthesized from the trigonal (α) $HfMo_2O_8$ by application of high pressures and high temperatures. The sample obtained is characterized by powder x-ray diffraction (XRD) and the details of high-pressure and high-temperature phase are explained. The Rietveld analysis of the powder XRD data reveals that the β-$HfMo_2O_8$ crystallizes in a monoclinic lattice with unit cell parameters $a=11.4138(6)$, $b=7.9105(4)$, $c=7.4395(3)$, Å and $\beta=122.35(0)^\circ$. The β-$HfMo_2O_8$ is found to be isostructural to the room-temperature phase of β-$ZrMo_2O_8$. The coordination numbers of Hf and Mo atoms with oxygen atoms are eight and five, respectively. The nature and sharing of Hf and Mo polyhedra are entirely different in β modification compared to that in the α phase.

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I. INTRODUCTION

Recently compounds having the framework structures, such as MX_2O_8 ($M=Zr^{4+}$ and Hf^{4+}) and $M'_2(XO_4)_3$ (M' $=$ trivalent cations, $X=Mo^{6+}$ and W^{6+}) have drawn considerable research interest due to their structural flexibility to facilitate the negative thermal expansion.[1,2] The compound ZrW_2O_8 is reported to exhibit a large isotropic negative thermal expansion over a wide temperature range (0.3–1050 K).[3] Such framework materials are used as components of the composites for attaining tunable thermal expansion values. The preparation and applications of these composites sometimes change the local pressures inside the composites, which may affect the stability of the above materials. Therefore, high-pressure studies of these negative thermal expansion materials have acquired a significant importance. Cubic ZrW_2O_8 undergoes an irreversible transformation to the orthorhombic phase at about 0.2 GPa, and amorphizes under further compression above 1.5 GPa.[4,5] Under the application of both pressure and temperature, the cubic ZrW_2O_8 transforms to an $\alpha-U_3O_8$ type phase.[6] $ZrMo_2O_8$ and $HfMo_2O_8$ in general do not crystallize in the cubic phase. However, they have cubic metastable modifications,[7,8] in which they show a negative thermal expansion behavior. $ZrMo_2O_8$ exists in a monoclinic lattice, which undergoes a reversible transition to the trigonal phase at about 913 K.[9] The monoclinic $ZrMo_2O_8$ (β form) (Ref. 10) is found to be denser than the high temperature, trigonal $ZrMo_2O_8$ (α form).[11] The trigonal (α) form is found to be the only stable modification as far as $HfMo_2O_8$ is concerned.[12]

The structural and phase evolution of α-$ZrMo_2O_8$ have been extensively studied at various pressures.[13–15] But no reports pertaining to the high pressure study on α-$HfMo_2O_8$, are available so far. Lind *et al.*[8] have reported that cubic (γ) $HfMo_2O_8$ undergoes a first order phase transition to a monoclinic modification on compression. But no detailed information of the high pressure phase is given. In this paper, we report the results of the high-pressure and high-temperature experiments carried out on α-$HfMo_2O_8$.

II. EXPERIMENT

Trigonal α-$HfMo_2O_8$ is prepared by a conventional solid state reaction of HfO_2 and MoO_3 at 650 °C for 18 h. The sample is reground and further heated at the same temperature for 8 h. The product thus obtained is characterized by powder x-ray diffraction (XRD) and found to consist of mainly trigonal $HfMo_2O_8$ (JC-PDS 38-1467) and a small amount of HfO_2 (JC-PDS 34-104). The high pressure and room temperature experiments are carried out on a Bridgman anvil apparatus (ϕ of face 12.7 mm),[16] in which the sample is pressed inside a pyrophilite gasket by two faces of the anvil. The sample is held at 7 GPa for 44 h and then retrieved after releasing the pressure. The high pressure and high temperature experiments are carried out on toroid anvil (TA) apparatus (ϕ of face 31 mm, ϕ of cavity 13.5 mm).[17] The powdered sample, pressed into a cylindrical pellet of approximately 4 mm diameter and 5.5-mm length, is encapsulated in a alumina (Al_2O_3) sample holder and placed at the center of a graphite heater assembly. The TA apparatus is pressure calibrated using Bi I - II and Yb hcp - bcc transitions at 2.65 and 4 GPa, respectively. In the experiments, the required pressure is attained gradually within a span of about 30 min. Thereafter the temperature is raised slowly at the rate of 10 °C/min. The pressurized sample is held at the required pressure and temperature for 10 min and then quenched by cutting off the heater power. The sample is retrieved by slowly releasing the pressure. The samples thus obtained are characterized by powder XRD, recorded on a Philips x-ray diffractometer (Model PW1710) with monochromatized Cu$K\alpha$ radiation, in the two-theta range of 10°–70°.

III. RESULTS AND DISCUSSIONS

All the observed reflections of the starting materials can be indexed on a trigonal lattice with the unit cell parameters: $a=10.100(1)$ and $c=11.738(1)$ Å, which are in agreement with the reported unit cell parameters: $a=10.1005$ and c $=11.7230$ Å.[9] This phase is iso-structural to α-$ZrMo_2O_8$

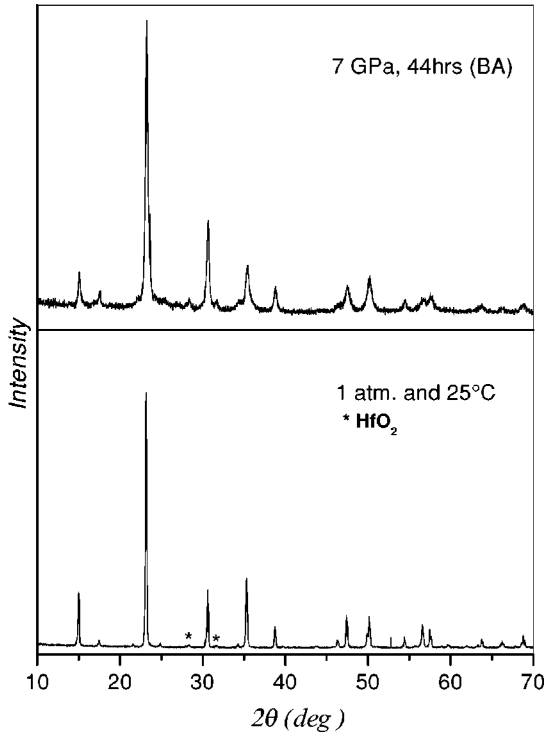

FIG. 1. (a) Powder XRD patterns of the original sample and (b) after compression in Bridgman anvil (BA) at 7 GPa, for 44 h.

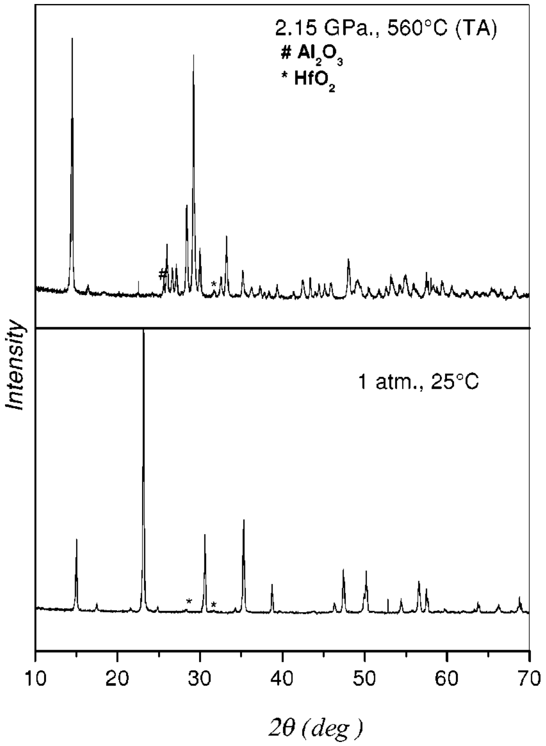

FIG. 2. (a) Powder XRD patterns of the original sample and (b) the retrieved sample from TA experiment at 2.15 GPa and 560 °C.

reported by Auray *et al.*[11] and Serezhkin *et al.*[18] The structure of the trigonal $ZrMo_2O_8$ or $HfMo_2O_8$ consists of ZrO_6 or HfO_6 octahedra, which share all the corners with the MoO_4 tetrahedra. Three of the MoO_4 tetrahedra apices are linked to ZrO_6 or HfO_6 octahedra, while the fourth apex points toward the interlayer region. This kind of framework arrangement of octahedra and tetrahedra makes this structure flexible and comparatively less dense. Such framework structures are highly amenable to transformations to denser phases on compression.

The XRD pattern of the product retrieved from the Bridgman anvil experiment is shown in Fig. 1. The XRD pattern of the starting material is also shown along with it for comparison. The XRD pattern of the retrieved sample shows a significant broadening of the reflections. However, there are no extra features observed, which indicates that there is no change in the unit cell type. The broadening of the reflections indicates that there is a tendency for this compound to undergo amorphization, which may be due to the nonhydrostatic conditions under pressure present in the Bridgeman anvil apparatus. The pressure induced amorphization (PIA) is a very common effect in such framework materials.[5,8] The present experiment indicates either the possibility of a reversible or kinetically sluggish amorphization in α-$HfMo_2O_8$. The onset pressure for PIA is reported for cubic $ZrMo_2O_8$ and cubic ZrW_2O_8 at 1.3 GPa (Ref. 8) and 1.5 GPa,[5] respectively, whereas the present compound, α-$HfMo_2O_8$ may amorphize at still higher pressures. A series of pressure induced reversible phase transitions, namely, monoclinic and triclinic are reported in the α-$ZrMo_2O_8$.[13,14] Since all these kinds of transitions are reversible, the present experimental method is not suitable to detect them, if they are present in the α-$HfMo_2O_8$.

To study the behavior of α-$HfMo_2O_8$ under the simultaneous application of pressure and temperature, the experiments are carried out on toroid anvil apparatus. Several trial experiments at different pressures and temperatures are carried out to find the optimum conditions for the phase transformation. The XRD pattern (Fig. 2) of the sample retrieved from 2.15 GPa and the 560 °C toroid anvil experiment shows the presence of completely new reflections, which could not be attributed to the starting trigonal phase, HfO_2 or MoO_3. This indicates the formation of a new phase of $HfMo_2O_8$, which hereafter will be referred as β-$HfMo_2O_8$. The XRD pattern of the starting material is also included in Fig. 2 for comparison.

A careful analysis of the XRD pattern indicates the presence of reflections attributable to the Al_2O_3 (corundum) phase, which is used as sample holder. The contamination of sample by the sample holder is often unavoidable due to the difficulty in the physical separation of the sample holder and the sample. All the observed reflections excluding the Al_2O_3 reflections can be indexed on a primitive monoclinic lattice with unit cell parameters: $a=9.729(2)$, $b=7.907(2)$, $c=7.435(1)$ Å, and $\beta=97.87(2)°$. These unit cell parameters are similar to those reported for monoclinic (β) $ZrMo_2O_8$.[9] In addition, a similar satisfactory indexing is possible with a C type monoclinic lattice with unit cell parameters: $a=11.415(3)$, $b=7.906(2)$, $c=7.438(2)$ Å, and $\beta=122.37(2)°$. Both the unit cells have equal volumes and indicate four formula units in the unit cell (i.e., $Z=4$). Similar two sets of unit cell parameters have been earlier assigned

TABLE I. The details of Rietveld refinement of β-HfMo$_2$O$_8$.

Phase	β-HfMo$_2$O$_8$
Preparation condition	2.15 GPa and 560 °C (quenched)
Data collection conditions	1 atm. and 25 °C
Crystal system	Monoclinic
Space group	$C2/c$ (No. 15)
a (Å)	11.4138(6)
b (Å)	7.9105(4)
c (Å)	7.4395(3)
β (°)	122.35(0)
V and ρ	567.45(5) Å^3, 5.83 gm/cm^3
Z	4
Wavelength (Å), Cu$K\alpha1$, and $\alpha2$	1.5406 and 1.5444
No. data points	2951
Two theta range	10-70°
Step width and step time	0.02° and 1.25 s.
No. of reflections	232/2
No of refined parameters	26
Rp, Rwp, Rexp	8.81%, 11.5%, 8.59%
χ^2	1.81
RBragg, RF	5.50%, 4.41%

TABLE II. Fractional atomic coordinates of various atoms in β-HfMo$_2$O$_8$.

Atom	Site	x	y	Z	B[a]
Hf	4e	0	0.9825 (5)	0.25	0.003
Mo	8f	0.2184(6)	0.2795(5)	0.2615(9)	0.005
O1	8f	0.082(2)	0.098(3)	0.073(4)	0.007
O2	8f	0.168(2)	0.161(3)	0.439(4)	0.008
O3	8f	0.349(2)	0.291(3)	0.226(4)	0.011
O4	8f	0.125(2)	0.454(3)	0.173(3)	0.018

[a] Fixed during the refinement.

to β-ZrMo$_2$O$_8$. However, these two unit cells are closely related.[9] High pressure studies on α-ZrMo$_2$O$_8$ reveal new phases, namely, monoclinic (δ) and triclinic (ϵ).[13–15] The structure of δ-ZrMo$_2$O$_8$ is related to the trigonal α-ZrMo$_2$O$_8$. The present observed monoclinic phase of HfMo$_2$O$_8$ is not similar to the monoclinic δ-ZrMo$_2$O$_8$. It may be mentioned here that the crystal structures of α- and β-ZrMo$_2$O$_8$ are not closely related, which indicates a reconstructive type phase transformation. The x-ray density of α and β modifications of HfMo$_2$O$_8$ are 4.79 and 5.84 gm/cm^3, respectively. Thus the density of the phase increases and the molecular volume decreases significantly from 172.8 to 141.7 Å^3, in the α to β transformation. This drastic change in the unit cell volume implies the possibility of a first order reconstructive type phase transition. A comparison of these volumes to that of the cubic HfMo$_2$O$_8$ (molar volume 190 Å^3),[8] shows that the α (trigonal) and β (monoclinic) modifications of HfMo$_2$O$_8$ are the denser phases.

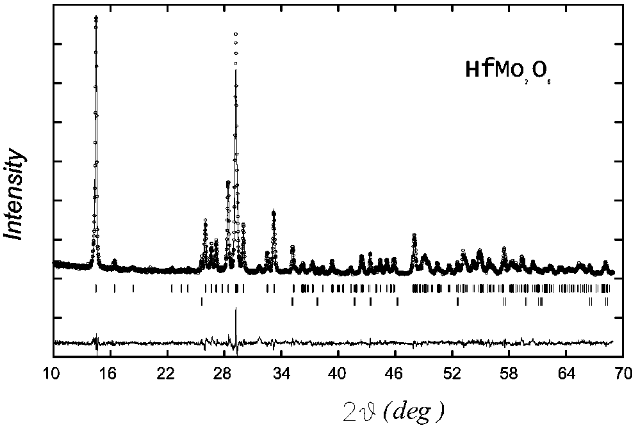

FIG. 3. The observed and calculated diffraction pattern for β-HfMo$_2$O$_8$. The difference plot is shown at the bottom. The vertical bars indicate the Bragg position of β-HfMo$_2$O$_8$ (upper) and α-Al$_2$O$_3$ (lower).

The detailed structural analysis of β-ZrMo$_2$O$_8$ is reported on the basis of the settings of the unit cell parameters $a = 11.433$, $b = 7.935$, $c = 7.460$ Å, and $\beta = 122.3°$.[10] A theoretical pattern calculated using the observed unit cell parameters of β-HfMo$_2$O$_8$ and the position coordinates of β-ZrMo$_2$O$_8$,[10] appears similar to the experimentally observed XRD pattern, which indicates that the β-HfMo$_2$O$_8$ is isostructural to β-ZrMo$_2$O$_8$. The structural analysis is carried out by Rietveld refinement using the FULLPROF-2K Rietveld refinement program.[19] The position coordinates and thermal parameters of the starting model are taken from β-ZrMo$_2$O$_8$.[10] Scale and background parameters are refined during the initial cycles of Rietveld refinements. The profile is fitted using pseudo-Vogt function. The half-width parameter, mixing parameters and unit cell parameters of both β-HfMo$_2$O$_8$ and Al$_2$O$_3$ phases are also refined. The preferred orientation correction is applied by Rietveld function option provided by FULLPROF package. Finally the position coordinates of both phases along with scale and unit cell parameters are refined. The goodness of the refinement is amply reflected from the observed R values (Table I). The observed and calculated profiles along with the difference plot are given in Fig. 3. It can be mentioned here that without refining the thermal parameters a good fit could be obtained. Further refinements of these thermal parameters are not successful, and hence they are kept fixed at their original values. The refined position parameters are given in Table II.

TABLE III. Typical interatomic distances (in Å) in β-HfMo$_2$O$_8$.

Hf		Mo	
O1	2.150(27)×2	O1	2.031(21)
O1	2.187(32)×2	O2	1.937(32)
O2	2.184(20)×2	O2	1.943(25)
O3	2.232(25)×2	O3	1.646(31)
		O4	1.650(23)
		-	-
Average	2.19	Average	1.84
		O4	3.02

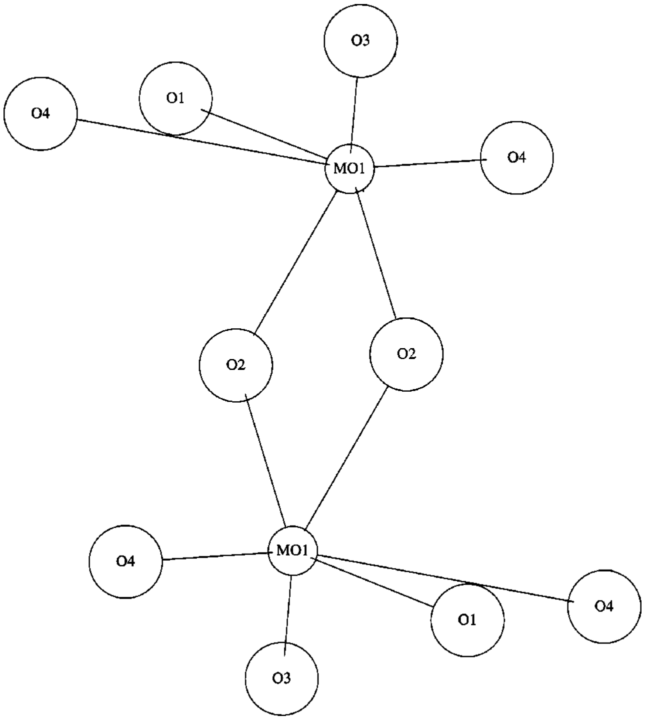

FIG. 4. A typical $[Mo_2O_8]^{4-}$ unit. The long Mo-O_4 bond is also shown.

The crystal structure of β-$HfMo_2O_8$ has only one kind of Hf and Mo atom each. There are four distinct oxygen atoms in the unit cell. The typical bond lengths of various atoms are given in Table III. The Hf atoms have eight coordinated polyhedra, which seems to be more regular compared to Zr polyhedra in β-$ZrMo_2O_8$. The Hf-O bond lengths range from 2.15 to 2.23 Å (average distance 2.19 Å). The corresponding Zr-O bond lengths in β-$ZrMo_2O_8$ range from 2.12 to 2.31 Å.[10] The Mo atoms have fivefold coordination polyhedra with Mo-O bond lengths ranging from 1.65 to 2.03 Å (average of 1.84 Å), which is close to a tetragonal pyramid. The corresponding Mo-O bond lengths in β-$ZrMo_2O_8$ are ranging from 1.68 to 2.04 Å. One O1 atom and, two O2 and O3 atoms form the distorted irregular tetragonal base of the tetragonal pyramid having O4 as the apex. The MoO_5 polyhedra can also be explained as a highly distorted octahedra considering O4 of another MoO_5 unit at a relatively longer distance (3.02 Å). Two such units are linked together by sharing O2-O2 basal edge forming a $[Mo_2O_8]^{4-}$ dimer, similar to that present in the β-$ZrMo_2O_8$ (Ref. 10) and $K_2Mo_3O_{10}$.[20] A typical dimer unit of $[Mo_2O_8]^{4-}$ with two long distance O4's is shown in Fig. 4. The HfO_8 polyhedra are linked together by sharing one edge forming infinite chains along the *c* direction. A typical chain of HfO_8 is shown in Fig. 5. A (010) projection of β-$HfMo_2O_8$ indicating the typical packing of the polyhedra is shown in Fig. 6. The HfO_8 chains and $[Mo_2O_8]^{4-}$ units are shown as dark gray and white polyhedrons, respectively. The HfO_8 polyhedra share two opposite O1-O2 edges with two different MoO_5 tetragonal pyramids. The O3 apex of MoO_5 tetragonal pyramid is connected to the HfO_8 polyhedra of another chain. Thus the $[Mo_2O_8]^{4-}$ units form the link between the HfO_8 chains. The O4 oxygen of MoO_5 unit is free and present inside the space between the $[Mo_2O_8]^{4-}$ units.

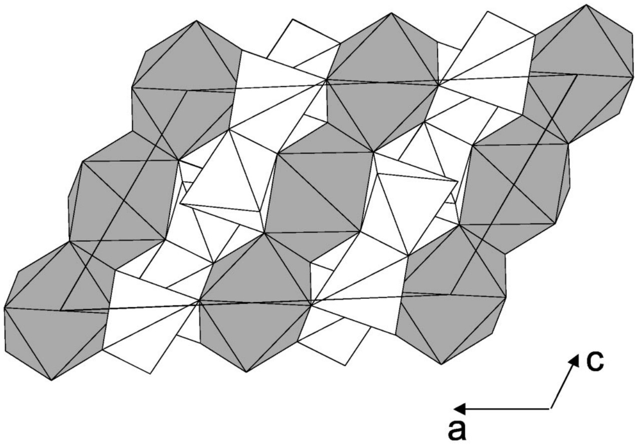

FIG. 6. Projection of β-$HfMo_2O_8$ along the [010] direction. The HfO_8 polyhedra (dark) and $[Mo_2O_8]^{4-}$ (white) are shown.

IV. CONCLUSIONS

In conclusion we report on a new polymorph of $HfMo_2O_8$ synthesized from high-pressure and high-temperature TA ex-

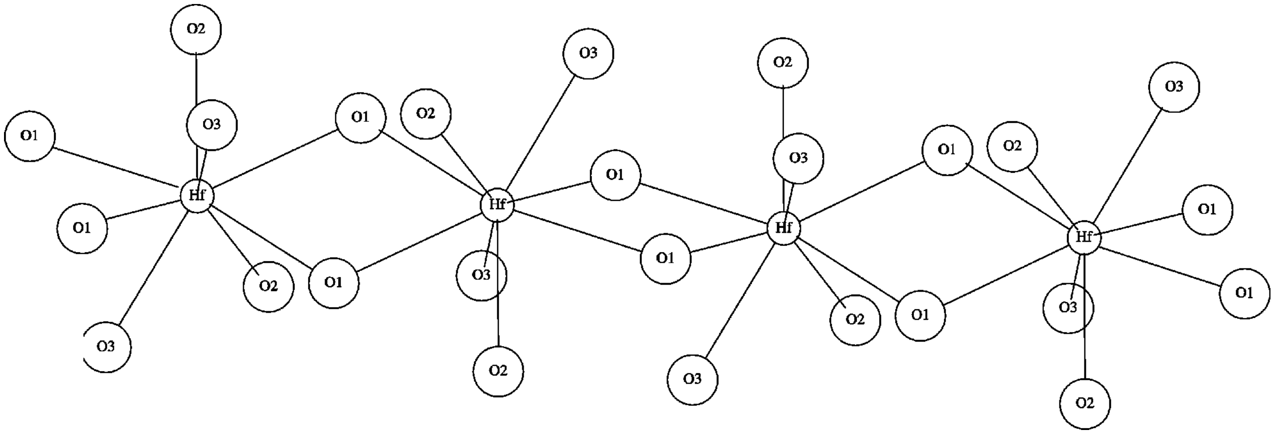

FIG. 5. A typical chain of HfO_8 polyhedra.

periments. The crystal structure of the phase is found to be isostructural to the monoclinic β-$ZrMo_2O_8$. The new β phase of $HfMo_2O_8$ is about 20% denser than the original α-$HfMo_2O_8$ suggesting a possibility of a first order phase transition. The room temperature high-pressure study of the trigonal $HfMo_2O_8$ up to 7 GPa indicates the absence of any irreversible phase transition. However, a tendency to amorphization is observed in this compound as against cubic $ZrMo_2O_8$ and ZrW_2O_8, which amorphize at much lower pressures.

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