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# Heats of Formation for Several Crystalline Polymorphs and Pressure-Induced Amorphous Forms of $AMo_2O_8$ (A = Zr, Hf) and $ZrW_2O_8$

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The enthalpies of drop solution ($\Delta H_{ds}$) for several polymorphs of $ZrW_2O_8$ (cubic, orthorhombic, trigonal, and amorphous), $ZrMo_2O_8$ (cubic, trigonal, monoclinic, and amorphous), and $HfMo_2O_8$ (cubic, trigonal, and amorphous) have been measured in molten $3Na_2O\cdot4MoO_3$ at 975 K. Using the values of $\Delta H_{ds}$ for the binary oxides, we calculated enthalpies of formation from the oxides at 298 K. Monoclinic $ZrMo_2O_8$ is the only polymorph examined that is enthalpically stable relative to the binary oxides ($\Delta H_{f,ox} = -5.1 \pm 3.5$ kJ/mol), and even that stability is marginal. The $\Delta H_{f,ox}$ values for cubic and trigonal $ZrMo_2O_8$ are $45.2 \pm 5.3$ and $32.2 \pm 4.5$ kJ/mol, respectively; for cubic and trigonal $HfMo_2O_8$, $55.8 \pm 3.1$, and $46.5 \pm 3.6$ kJ/mol, respectively; and for cubic, orthorhombic, and trigonal $ZrW_2O_8$, $64.8 \pm 2.8$, $50.6 \pm 3.0$, and $49.8 \pm 4.1$ kJ/mol, respectively. Therefore, these phases are either entropically stabilized and/or their formation/persistence is kinetically controlled. The enthalpies of formation from the oxides, at ambient pressure, for the amorphous phases recovered after compression of the cubic polymorphs in a multianvil press are more positive than those of the crystalline polymorphs: $98.9 \pm 5.0$ kJ/mol for $ZrMo_2O_8$, $102.0 \pm 6.3$ kJ/mol for $HfMo_2O_8$, and $127.8 \pm 5.5$ kJ/mol for $ZrW_2O_8$. The entropies of the amorphous phases are probably greater than those for the cubic ones and thus the pressure-induced amorphous phase can be entropically (as well as volumetrically) favored, and the pressure-induced amorphization boundary probably has a negative $P-T$ slope. Nevertheless, these amorphous phases could be metastable with respect to more dense crystalline polymorphs, either in the P−T range where they are observed or at higher pressure.

## Introduction

The family of cubic $AM_2O_8$ compounds (A = Hf, Zr; M = Mo, W) has recently received considerable attention, as they all exhibit negative thermal expansion (NTE).[1−5] In contrast to most other NTE materials, the expansion behavior is isotropic and occurs over a large temperature range, including at room temperature. NTE materials have potential applications in composites, as they can be used to tailor the overall expansion coefficient of the material.[6,7]

At ambient conditions, all of these cubic compounds are metastable with respect to the binary oxides.[2,5] To date, only the cubic tungstates are known to be thermodynamically stable at high temperatures (∼1400−1500 K),[2] whereas the corresponding cubic molybdates seem to be metastable at all temperatures.[5] The cubic tungstates and molybdates of Zr and Hf are isostructural and show very similar characteristics.[3,8,9] In addition, each compound can exist in two or three different crystalline polymorphic forms at ambient conditions.[4,5,10,11] Amorphous phases of $AM_2O_8$ composition have been obtained by compression of the cubic phases.[12−18]

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(1) Martinek, C.; Hummel, F. A. *J. Am. Ceram. Soc.* **1968**, *51*, 227.
(2) Mary, T. A.; Evans, J. S. O.; Vogt, T.; Sleight, A. W. *Science* **1996**, *272*, 90.
(3) Evans, J. S. O.; Mary, T. A.; Vogt, T.; Subramanian, M. A.; Sleight, A. W. *Chem. Mater.* **1996**, *8*, 2809.
(4) Evans, J. S. O.; Hu, Z.; Jorgensen, J. D., Argyriou, D. N.; Short, S.; Sleight, A. W. *Science* **1997**, *275*, 61.
(5) Lind, C.; Wilkinson, A. P.; Hu, Z.; Short, S.; Jorgensen, J. D. *Chem. Mater.* **1998**, *10*, 2335.
(6) Fleming, D. A.; Johnson, D. W.; Lemaire, P. J. US Patent 5 694 503; Lucent Technologies, Murray Hill, NJ, 1997.
(7) Fleming, D. A.; Lemaire, P. J.; Johnson, D. W. European Patent EP 97−306798 19970902; Lucent Technologies, Murray Hill, NJ, 1998.
(8) Jorgensen, J. D.; Hu, Z.; Short, S.; Sleight, A. W.; Evans, J. S. O. *J. Appl. Phys.* **2001**, *89*, 3184.
(9) Lind, C.; VanDerveer, D. G.; Wilkinson, A. P.; Chen, J.; Vaughan, M. T.; Weidner, D. J. *Chem. Mater.* **2001**, *13*, 487.
(10) Wilkinson, A. P.; Lind, C.; Pattanaik, S. *Chem. Mater.* **1999**, *11*, 101.
(11) Auray, M.; Quarton, M.; Tarte, P. *Powder Diffr.* **1987**, *2*, 36.
(12) Perottoni, C. A.; de Jornada, J. A. H. *Science* **1998**, *280*, 886.
(13) Ravindran, T. R.; Arora, A. K.; Mary, T. A. *Phys. Rev. Lett.* **2000**, *84*, 3879.
(14) Ravindran, T. R.; Arora, A. K.; Mary, T. A. *J. Phys.: Condens. Matter* **2001**, *13*, 11573.
(15) Grzechnik, A.; Crichton, W. A.; Syassen, K.; Adler, P.; Mezouar, M. *Chem. Mater.* **2001**, *13*, 4255.
(16) Grzechnik, A.; Crichton, W. A. *Solid State Sci.* **2002**, *4*, 1137.
(17) Varga, T.; Wilkinson, A. P.; Jupe, A. C.; Lind, C.; Bassett, W. A.; Zha, C.-S. *Phys. Rev. B* **2005**, *72*, 24117.
(18) Varga, T.; Wilkinson, A. P.; Lind, C.; Bassett, W. A.; Zha, C.-S. *Solid State Commun.* **2005**, *135*, 739.

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**Table 1. Synthesis and Stability Range for the Studied Polymorphs of $ZrMo_2O_8$, $HfMo_2O_8$, and $ZrW_2O_8$**

| material | conditions of formation | reported range of stability |
|---|---|---|
| cubic $ZrMo_2O_8$ | dehydration of $ZrMo_2O_7(OH)_2{\cdot}2H_2O$ at 623−663 K[5] | 0 to ~1 (0.7−2.0) GPa,[9,16] 0−660 K[5] |
| trigonal $ZrMo_2O_8$ | from the oxides at 973 K or from the cubic phase by prolonged heating at 663 K[5] | 0 to ~1 GPa[58−60] (forms a monoclinic phase different from the one below at ~1.1 GPa); $T > 952$ K[11] |
| monoclinic $ZrMo_2O_8$ | from the oxides by heating at 923 K for 3 months or heating to ≥818 K at 1.3 GPa or ≤1063 K under 1.3−4.0 GPa[16] | decomposes when heated to 1013 K at >4 GPa[16] |
| amorphous $ZrMo_2O_8$ | compression at 1.5−4 GPa or higher (RT)[16, 18] | monoclinic when heated to 898 K at 3.2 GPa, decomposes when heated to 1013 K at >4 GPa[16] |
| cubic $HfMo_2O_8$ | dehydration of $HfMo_2O_7(OH)_2{\cdot}2H_2O$ at 623−663 K[5] | 0 to ~1 (0.7−2.0) GPa,[9] 0−660 K |
| trigonal $HfMo_2O_8$ | from the oxides at 923 K[63] or from cubic by long heating at 663 K | monoclinic when heated to 833 K at ~2 GPa[63] |
| amorphous $HfMo_2O_8$ | compression at above 4 GPa (RT) | crystallization to trigonal starts at 473 K |
| cubic $ZrW_2O_8$ | from the oxides at 1423 K | 0−0.2 GPa,[4] 0.3−1050 K[2] and 1380−1530 K[64] |
| orthorhombic $ZrW_2O_8$ | from cubic at 0.2−0.6 GPa[4] | transforms to cubic at 393 K[4] |
| trigonal $ZrW_2O_8$ | non-hydrolytic sol−gel route[10] | decomposes on prolonged heating at 1023 K |
| amorphous $ZrW_2O_8$ | compression at 2.5−5.0 GPa or higher (RT)[17] | crystallization to cubic phase at 925 K[39] |

Table 1 (with references therein) summarizes the conditions for the formation of the different $AM_2O_8$ polymorphs. Trigonal $ZrMo_2O_8$, trigonal $HfMo_2O_8$, and cubic $ZrW_2O_8$ can be made directly from the binary oxides, although the trigonal $HfMo_2O_8$ sample in this study was prepared by dehydration of a precursor. Monoclinic $ZrMo_2O_8$ can also be prepared from the binary oxides, but its formation appears to be kinetically hindered and requires extended heating (several months at ambient pressure). Cubic $ZrMo_2O_8$ and cubic $HfMo_2O_8$ have only been prepared by dehydration of $AMo_2O_7(OH)_2{\cdot}2H_2O$, whereas trigonal $ZrW_2O_8$ has only been obtained via non-hydrolytic sol−gel chemistry. The amorphous materials as well as orthorhombic $ZrW_2O_8$ can be prepared by compression.

Since the amorphization of hexagonal ice under compression has been reported,[19] pressure-induced amorphization (PIA) has been observed for many different materials.[20−29] The phenomenon is not uncommon for open framework structures and occurs at relatively low pressures in several NTE materials.[9,12,16,29,30] A possible theoretical link between NTE and PIA has been suggested.[31] Several different structural mechanisms have been proposed for PIA, some of which are related or can operate simultaneously.[22,24,25,31−33] Typically, the amorphous phase produced on compression is viewed as a metastable intermediate between the low-pressure crystalline phase and the high-pressure thermodynamic equilibrium products.[24,25] PIA in NTE materials is not purely of academic interest; the changes in expansion characteristics that accompany it can be detrimental to applications as the processing or use of composites may involve high pressures.[34−36] Although the mechanism of PIA in cubic $ZrW_2O_8$,[12,14,15,17,37] cubic $ZrMo_2O_8$,[16,18] and some other NTE materials[29,30,38] has been studied, very little is known about the relative thermodynamic stability of crystalline and amorphous phases of NTE materials. A recent study suggests a positive enthalpy change and therefore an increase in entropy in the amorphous to crystalline (cubic) phase transition in $ZrW_2O_8$.[39] This counterintuitive behavior was inferred from endothermic recrystallization seen by differential thermal analysis (DTA) and rationalized by postulating that increased vibrational entropy in the crystalline material overrides the loss of configurational entropy.

There are no literature reports of enthalpies of formation ($\Delta H_f$) or Gibbs free energies of formation ($\Delta G_f$) for any of the $AM_2O_8$ polymorphs with the exception of trigonal $AMo_2O_8$, where $\Delta H_f$ and $\Delta G_f$ have been estimated using isoperibol solution calorimetry,[40−42] $\Delta G_f$ and $\Delta G_{f,ox}$ by the transpiration technique[43,44] and $\Delta H_f$, $\Delta G_f$, and $\Delta G_{f,ox}$ by the EMF method.[45−47] As both thermodynamic and kinetic factors determine which polymorphs of $AM_2O_8$ can be obtained using a given synthetic method and under which conditions decomposition to the binary oxides will occur, an understanding of the thermodynamics in this system is of value. In addition, knowing the energetics for

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(19) Mishima, O.; Calvert, L. D.; Whalley, E. *Nature* **1984**, *310*, 393.
(20) Hemley, R. J.; Jephcoat, A. P.; Mao, H. K.; Ming, L. C.; Manghnani, M. H. *Nature* **1988**, *334*, 52.
(21) Kruger, M. B.; Jeanloz, R. *Science* **1990**, *249*, 647.
(22) Ponyatovsky, E. G.; Barkalov, O. I. *Mater. Sci. Rep.* **1992**, *8*, 147.
(23) Jayaraman, A.; Sharma, S. K.; Wang, Z.; Wang, S. Y.; Ming, L. C.; Manghnani, M. H. *J. Phys. Chem. Solids* **1993**, *54*, 827.
(24) Sharma, S. M.; Sikka, S. K. *Prog. Mater. Sci.* **1996**, *40*, 1.
(25) Richet, P.; Gillet, P. *Eur. J. Mineral.* **1997**, *9*, 907.
(26) Badro, J.; Gillet, P.; Barrat, J.-L. *Europhys. Lett.* **1998**, *42*, 643.
(27) Sakuntala, T.; Arora, A. K.; Chandra Shekar, N. V.; Sahu, P. C. *J. Phys.: Condens. Matter* **2000**, *12*, 4417.
(28) Dmitriev, V.; Sinitsyn, V.; Dilanian, R.; Machon, D.; Kuznetsov, A.; Ponyatovsky, E.; Lucazeau, G.; Weber, H. P. *J. Phys. Chem. Solids* **2003**, *64*, 307.
(29) Liu, H.; Secco, R. A.; Imanaka, N.; Adachi, G. *Solid State Commun.* **2002**, *121*, 177.
(30) Secco, R. A.; Liu, H.; Imanaka, N.; Adachi, G. *J. Mater. Sci. Lett.* **2001**, *20*, 1339.
(31) Speedy, R. J. *J. Phys. Condens. Matter* **1996**, *8*, 10907.
(32) Yamanaka, T.; Nagai, T.; Tsuchiya, T. *Z. Kristallogr.* **1997**, *212*, 401.
(33) Arora, A. K. *Solid State Commun.* **2000**, *115*, 665.
(34) Verdon, C.; Dunand, D. C. *Scr. Mater.* **1997**, *36*, 1075.
(35) Holzer, H.; Dunand, D. C. *J. Mater. Res.* **1999**, *14*, 780.
(36) Balch, D. K.; Dunand, D. C. *Metall. Mater. Trans. A* **2004**, *35A*, 1159.
(37) Pereira, A. S.; Perottoni, C. A.; de Jornada, J. A. H. *J. Raman Spectrosc.* **2003**, *34*, 578.
(38) Arora, A. K.; Nithya, R.; Yagi, T.; Miyajima, N.; Mary, T. A. *Solid State Commun.* **2004**, *129*, 9.
(39) Perottoni, C. A.; Zorzi, J. E.; da Jornada, J. A. H. *Solid State Commun.* **2005**, *134*, 319.
(40) Bharadwaj, S. R.; Dharwadkar, S. R.; Samat, M. S. *J. Nucl. Mater.* **1994**, *211*, 244.
(41) Bharadwaj, S. R.; Samant, M. S.; Mishra, R.; Dharwadkar, S. R.; Savant, S. S.; Kalyanaraman, R. *J. Alloys Compd.* **1995**, *230*, 13.
(42) Bharadwaj, S. R.; Samant, M. S.; Mishra, R.; Dharwadkar, S. R.; Sawant, S. S.; Kalyanaraman, R. *Thermochim.Acta* **1997**, *296*, 11.
(43) Samant, M. S.; Bharadwaj, S. R.; Kerkar, A. S.; Dharwadkar, S. R. *J. Nucl. Mater.* **1993**, *200*, 157.
(44) Samant, M. S.; Bharadwaj, S. R.; Kerkar, A. S.; Dharwadkar, S. R. *J. Nucl. Mater.* **1993**, *207*, 98.
(45) Singh, Z.; Dash, S.; Prasad, R.; et al. *J. Alloys Compd.* **1996**, *244*, 85.
(46) Pankajavalli, R.; Sreedharan, O. M. *J. Nucl. Mater.* **1990**, *172*, 151.
(47) Pankajavalli, R.; Sreedharan, O. M. *J. Nucl. Mater.* **1990**, *175*, 194.

**Table 2. Sample Naming Scheme and Results of Drop Solution Calorimetry**[a]

| sample no. | material | no. of pellets | $\Delta H_{ds}$ (kJ/mol) | $\Delta H_{f,ox}$ (kJ/mol) from oxides | $\Delta H_{f,el}$ (kJ/mol) from elements | molar volume ($cm^3$/mol) |
|---|---|---|---|---|---|---|
| 1 | $ZrO_2$[65] | 9 | 19.7 ± 1.8 | 0 | −1097.46[51] | 21.1 |
| 2 | $HfO_2$[66] | 23 | 20.0 ± 2.2 | 0 | −1150.64[51] | 20.8 |
| 3 | $WO_3$ | 8 | 91.68 ± 1.34 | 0 | −842.91[51] | 31.9 |
| 4 | $MoO_3$ | 12 | 76.21 ± 1.47 | 0 | −745.17[51] | 32.0 |
| 5 | cub. $ZrMo_2O_8$ | n/a | 128.35 ± 2.17 | 43.77 ± 3.18 | −2544.03 ± 3.18 | 114.6 |
| 6 | cub. $ZrMo_2O_8$ | 10 | 125.57 ± 3.52 | 46.55 ± 4.22 | −2541.25 ± 3.64 | 114.6 |
| 5−6 | average for cub. $ZrMo_2O_8$ | n/a | | 45.16 ± 5.28 | −2542.64 ± 4.13 | 114.6 |
| 7 | trig. $ZrMo_2O_8$ | 10 | 141.65 ± 2.34 | 30.47 ± 3.30 | −2557.33 ± 3.30 | 104.7 |
| 8 | trig. $ZrMo_2O_8$ | 6 | 138.17 ± 2.01 | 33.95 ± 3.07 | −2553.85 ± 3.07 | 104.7 |
| 7−8 | average for trig. $ZrMo_2O_8$ | n/a | | 32.21 ± 4.51 | −2555.59 ± 4.51 | 104.7 |
| 9 | mono. $ZrMo_2O_8$ | 9 | 177.25 ± 2.6 | −5.13 ± 3.49 | −2592.93 ± 3.49 | 86.2 |
| 10 | am. $ZrMo_2O_8$ | 4 | 73.19 ± 4.37 | 98.93 ± 4.95 | −2488.87 ± 6.42 | |
| 11 | cub. $HfMo_2O_8$ | 6 | 116.67 ± 1.56 | 55.75 ± 3.07 | −2585.23 ± 2.96 | 114.4 |
| 12 | trig. $HfMo_2O_8$ | 9 | 125.91 ± 2.43 | 46.51 ± 3.59 | −2594.47 ± 3.59 | 104.2 |
| 13 | am. $HfMo_2O_8$ | 4 | 87.95 ± 5.76 | 101.99 ± 6.34 | −2556.51 ± 7.06 | |
| 14 | cub. $ZrW_2O_8$ | 7 | 138.24 ± 1.60 | 64.82 ± 2.76 | −2718.46 ± 2.76 | 115.6 |
| 15 | ortho. $ZrW_2O_8$ | 8 | 152.41 ± 2.07 | 50.65 ± 3.05 | −2732.63 ± 3.05 | 109.6 |
| 16 | trig. $ZrW_2O_8$ | 10 | 153.29 ± 3.48 | 49.77 ± 4.14 | −2733.51 ± 4.14 | 98.2 |
| 17 | am. $ZrW_2O_8$ | 7 | 75.30 ± 5.02 | 127.76 ± 5.50 | −2655.52 ± 7.03 | |

[a] Errors in the heats of dissolution and heats of formation are given as two standard deviations of the mean. Enthalpies of formation from the elements and molar volumes are also shown for reference. Heats of dissolution for $MoO_3$ and $WO_3$ were measured in this work, values for $ZrO_2$ and $HfO_2$ were determined previously at the Thermochemistry Facility at UC Davis.[65,66] Synthesis methods: samples 5 and 6, dehydration of $ZrMo_2O_7(OH)_2{\cdot}2H_2O$; 7, solid-state reaction; 8, heating sample 5; 9, solid-state reaction; 11, 12, dehydration of of $HfMo_2O_7(OH)_2{\cdot}2H_2O$; 14, solid-state reaction at 1200 °C; 15, from sample 13 by compression to 0.6 GPa; 16, non-hydrolytic sol−gel chemistry; 10, 13, and 17, high-pressure synthesis at 7.5 GPa and RT.

the pressure-induced amorphous phases relative to the crystalline starting materials as well as the binary oxides will help us better understand the occurrence and mechanism of PIA.

Calorimetric measurements of heats of formation are complicated by the difficulty of dissolving $AM_2O_8$ in all common acids and bases and the materials' metastability. Solution calorimetry in molten oxide solvents at 975−1075 K overcomes the problems of slow dissolution in aqueous solvents. Here, we report the measurement of heats of formation (from binary oxides) of various polymorphs of $ZrMo_2O_8$, $HfMo_2O_8$, and $ZrW_2O_8$ through thermochemical cycles involving drop solution calorimetry (sample dropped from room temperature into the hot melt) of these phases in molten $3Na_2O{\cdot}4MoO_3$ at 975 K.

## Experimental Section

**Syntheses.** Table 2 shows the samples used in this study. Cubic $ZrMo_2O_8$ (samples 5 and 6) was synthesized by the careful dehydration of $ZrMo_2O_7(OH)_2{\cdot}2H_2O$, which was prepared using a modification of our previously described procedure.[5] The precursor materials were $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (J. T. Baker, Phillipsburg, NJ) and either $ZrOCl_2{\cdot}xH_2O$ (Alfa Aesar, Ward Hill, MA) and HCl (J. T. Baker, Phillipsburg, NJ) (sample 5) or $ZrO(ClO_4)_2{\cdot}xH_2O$ (Aldrich, Milwaukee, WI) and $HClO_4$ (Fisher Scientific, Fair Lawn, NJ) (sample 6). Trigonal $ZrMo_2O_8$ was obtained by heating sample 5 at 973 K (sample 7), and another sample was prepared by reaction of a stoichiometric mixture of the binary oxides at 973 K (sample 8). Monoclinic $ZrMo_2O_8$ (sample 9) was obtained by heating a stoichiometric mixture of $ZrO_2$ (Alfa Aesar, Ward Hill, MA) and $MoO_3$ (J. T. Baker, Phillipsburg, NJ) to 923 K for 3 months.

Cubic and trigonal $HfMo_2O_8$ (samples 11−12) were prepared by dehydration of $HfMo_2O_7(OH)_2{\cdot}2H_2O$ that had been synthesized using the same procedure as that used for $ZrMo_2O_8$ with $HfOCl_2{\cdot}xH_2O$ (Alfa Aesar, Ward Hill, MA), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Alfa Aesar, Ward Hill, MA), and HCl (Fisher Scientific, Fair Lawn, NJ) as starting materials.

Cubic $ZrW_2O_8$ was prepared from a stoichiometric mixture of $ZrO_2$ and $WO_3$ by heating at 1423 K (sample 14). A part of sample 14 was converted to orthorhombic $ZrW_2O_8$ by compression at 0.6 GPa in a He-gas pressure cell at the Intense Pulsed Neutron Source of the Argonne National Laboratory, Argonne, IL (sample 15). Trigonal $ZrW_2O_8$ (sample 16) was synthesized by a non-hydrolytic sol−gel route.[10]

The materials prepared by solid-state reaction from the oxides did not show any significant weight loss on firing. Therefore, the final stoichiometry was assumed to be the same as that of the starting mixtures of predried oxides, with no additional volatiles adsorbed.

All amorphous samples (samples 10, 13, and 17) were prepared by compressing the corresponding cubic materials in a Walker-type high-pressure multianvil press[48] at the Department of Geology, UC Davis, Davis, CA. The pressure cell consisted of a Pt sample capsule in a 14 mm MgO octahedron surrounded by eight one-inch WC cubes, all truncated on the corner facing the MgO. About 100 mg of cubic sample was placed into the Pt capsule and exposed to a pressure of about 7.5 GPa at room temperature for 2 h prior to slow decompression.

**Characterization.** The structures of the crystalline samples were confirmed by X-ray diffraction (XRD) on either a Scintag X1 or a Scintag PAD V diffractometer with Cu Kα radiation operated at 45 kV and 40 mA. Lack of long-range order in the amorphous samples was confirmed by X-ray diffraction carried out on an Inel diffractometer (XRG 3000) at 30 kV and 30 mA using Cu Kα radiation. Samples were phase pure, with the exception of the monoclinic $ZrMo_2O_8$ (sample 9), which contained a trace amount of trigonal material, and the trigonal $ZrW_2O_8$ (sample 16), which contained a small amount of $WO_3$. All three amorphous phases were confirmed to have no detectable crystalline phases by X-ray diffraction.

Thermogravimetric analysis proved to be a very sensitive method for the elemental analysis of the molybdates. $MoO_3$ is volatile at high temperatures and evaporates above 1023 K. Ternary or

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(48) Walker, D.; Carpenter, M. A.; Hitch, C. M. *Am. Mineral.* **1990**, *75*, 1020.

quaternary compounds, however, are often stable to higher temperatures. In the case of $ZrMo_2O_8$, excess $MoO_3$ can be distinguished from that in the framework, as the excess evaporates around 1023 K, whereas the framework molybdenum is lost above 1200 K. The stoichiometries of the molybdate samples were determined by measuring the evaporation of $MoO_3$ at high-temperature using thermogravimetric analysis (TGA) on a Seiko thermal analysis module. A heating rate of 20 K/min from room temperature to 1473 K and a nitrogen gas flow rate of 150 mL/min were employed for the TGA analyses.

$ZrMo_2O_8$ and $HfMo_2O_8$ are insoluble in all common acids and bases, whereas $MoO_3$ is easily soluble even in dilute base. This allowed us to attempt the removal of excess $MoO_3$ in two of our calorimetric samples (11 and 12 in Table 2) by washing with 0.05 M NaOH. Subsequent XRD and TGA analyses confirmed that stoichiometric samples of the desired $AMo_2O_8$ polymorph were formed. However, $AMo_2O_8$ samples could contain amorphous material after synthesis or NaOH washing. By amorphous content in the ambient pressure crystalline samples, we mean a material that did not crystallize under the synthesis conditions or that consists of very small crystalline domains and is therefore amorphous to X-rays.

The mass fraction of water present in the amorphous $HfMo_2O_8$ sample (the only amorphous sample available in sufficient quantity for such analysis) and the amorphous to crystalline phase transition were analyzed by TGA/DSC using a Netzsch STA 449 system. The heating rate was 10 K/min to 1000 K, and dry Ar was used as a purge gas.

**Calorimetric Measurements.** The calorimetric experiments were carried out using a Tian-Calvet twin microcalorimeter[49,50] with sodium molybdate ($3Na_2O{\cdot}4MoO_3$) as a solvent. Enthalpies of drop solution were measured by dropping ~5 or ~15 mg pellets (depending on the available sample quantity) from room temperature into the solvent at 975 K. The calorimeter was calibrated with 5 and 15 mg pellets of $\alpha$-$Al_2O_3$. Ex situ experiments were carried out in a 975 K furnace. Several experiments were repeated by dropping 15 mg samples into a crucible containing molten sodium molybdate. After cooling, the sodium molybdate was dissolved in deionized water. No undissolved residual material was found for any of the samples. These trials confirmed that all samples were completely dissolved in the sodium molybdate solvent within 15 min. The samples were dried before the experiments and kept in a desiccator. The low-temperature cubic samples, which absorb water rapidly, were pressed into pellets in an argon-filled glove box equipped with a molecular sieve to absorb any water. The methodology was the same as that used previously for other ternary oxides.[49,50]

## Results

Enthalpies of drop solution along with the enthalpies of formation from the binary oxides are presented in Table 2. Enthalpies of formation from the elements and molar volumes are also shown in the table for reference. The measured heat effect consists of the heat content of the sample from room temperature to 975 K and the heat of solution in the solvent. Enthalpies of formation ($\Delta H_{f,\,ox}$) from the binary oxides at 298 K can be calculated from the following thermochemical cycle

$$AO_2\text{ (solid, 298 K)} + 2MO_3\text{ (solid, 298 K)} \rightarrow AM_2O_8\text{ (solid, 298 K)}\ \Delta H_{f,\,ox}$$

$$AO_2\text{ (solid, 298 K)} \rightarrow AO_2\text{ (dissolved, 975 K)}\ \Delta H_1$$

$$MO_3\text{ (solid, 298 K)} \rightarrow MO_3\text{ (dissolved, 975 K)}\ \Delta H_2$$

$$AM_2O_8\text{ (solid, 298 K)} \rightarrow AO_2\text{ (dissolved, 975 K)} + 2MO_3\text{ (dissolved, 975 k)}\ \Delta H_3$$

$$\Delta H_{f,ox} = \Delta H_1 + 2\Delta H_2 - \Delta H_3$$

The enthalpies of formation from the elements ($\Delta H_{f,el}$) were calculated using the following thermochemical cycle

$$A\text{ (solid, 298 K)} + 2M\text{ (solid, 298 K)} + 4O_2\text{ (gas, 298 K)} \rightarrow AM_2O_8\text{ (solid, 298 K)}\ \Delta H_{f,\,el}$$

$$AO_2\text{ (solid, 298 K)} \rightarrow AO_2\text{ (dissolved, 975 K)}\ \Delta H_1$$

$$MO_3\text{ (solid, 298 K)} \rightarrow MO_3\text{ (dissolved, 975 K)}\ \Delta H_2$$

$$AM_2O_8\text{ (solid, 298 K)} \rightarrow AO_2\text{ (dissolved, 975 K)} + 2MO_3\text{ (dissolved, 975 k)}\ \Delta H_3$$

$$A\text{ (solid, 298 K)} + O_2\text{ (gas, 298 K)} \rightarrow AO_2\text{ (solid, 298 K)}\ \Delta H_4$$

$$M\text{ (solid, 298 K)} + 1.5O_2\text{ (gas, 298 K)} \rightarrow MO_3\text{ (solid, 298 K)}\ \Delta H_5$$

$$\Delta H_{f,el} = \Delta H_1 + 2\Delta H_2 - \Delta H_3 + \Delta H_4 + 2\Delta H_5$$

The enthalpies of formation from the binary oxides are graphically displayed in Figure 1. The values for the two cubic $ZrMo_2O_8$ samples, 43.8 ± 3.2 and 46.6 ± 4.2 kJ/mol (samples 5 and 6), agree within experimental error. The values for the two trigonal samples (samples 7 and 8), 30.5 ± 3.3 and 34.0 ± 3.1 kJ/mol, are also in agreement. This shows that the preparation method does not have a significant effect on the heat of formation of the sample. The observed small difference, if real, might be related to the larger surface area of sample 8. Monoclinic $ZrMo_2O_8$ is the only phase with a negative enthalpy of formation, −5.1 ± 3.5 kJ/mol, whereas amorphous $ZrMo_2O_8$ has a significantly more positive enthalpy of formation than any of the three crystalline polymorphs (98.9 ± 5.0 kJ/mol).

The enthalpy of formation from the binary oxides of the $ZrMo_2O_8$ polymorphs becomes more endothermic from monoclinic (−5.1 ± 3.5 kJ/mol) to trigonal (32.2 ± 4.5 kJ/mol) to cubic (45.2 ± 5.3 kJ/mol) and to amorphous $ZrMo_2O_8$ (98.9 ± 5.0 kJ/mol). In the case of the $HfMo_2O_8$ polymorphs, it also becomes more endothermic from trigonal (46.5 ± 3.6 kJ/mol) to cubic (55.8 ± 3.1 kJ/mol) and to amorphous $HfMo_2O_8$ (102.0 ± 6.3 kJ/mol). Cubic (sample 14), orthorhombic (sample 15), trigonal (sample 16), and amorphous $ZrW_2O_8$ gave $\Delta H_{f,ox}$ values of 64.8 ± 2.8, 50.6 ± 3.0, 49.8 ± 4.1, and 127.8 ± 5.5 kJ/mol, respectively.

Rietveld analyses were carried out on a mixture of known quantities of cubic $ZrMo_2O_8$ (samples 5 and 6) and $Y_2O_3$, as well as cubic $HfMo_2O_8$ (sample 11) and $Y_2O_3$. $Y_2O_3$ was used as an internal standard. The commercial $Y_2O_3$ sample was assumed to be 100% crystalline. Its X-ray diffraction

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(49) Navrotsky, A. *Phys. Chem. Miner.* **1977**, *2*, 89.
(50) Navrotsky, A. *Phys. Chem. Miner.* **1997**, *24*, 222.

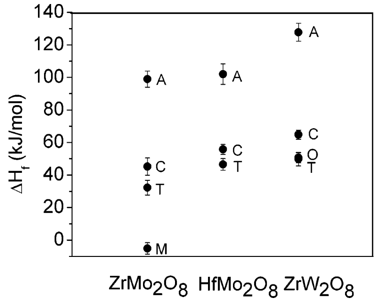

**Figure 1.** Enthalpies of formation from the binary oxides at 298 K for cubic (C), trigonal (T), monoclinic (M), and amorphous (A) $ZrMo_2O_8$; cubic, trigonal, and amorphous $HfMo_2O_8$, as well as cubic, orthorhombic (O), trigonal, and amorphous $ZrW_2O_8$.

peaks are sharp, and there is no "hump" in the pattern at low angle. The quantitative phase analyses indicated that the first cubic $ZrMo_2O_8$ sample (sample 5) contained 8 ± 1% of noncrystalline material, the second one (sample 6) contained 5.5 ± 0.5% amorphous material, and cubic $HfMo_2O_8$ (sample 11) contained 8 ± 1% of an amorphous phase. The amorphous phase in the ambient pressure crystalline samples may be different from those resulting from pressure-induced amorphization, which are denser and may be of different structure. If we assume that this amorphous material is energetically identical to the pressure-amorphized phase and correct the enthalpies of formation from the oxides of the above cubic phases using the heats of drop solution for the corresponding pressure-amorphized phases, we get $\Delta H_{f,ox}$ values slightly less endothermic than those in Table 2 (39.0 instead of 43.8 kJ/mol for sample 5, 43.5 instead of 46.6 kJ/mol for sample 6. and 53.2 instead of 55.6 kJ/mol for sample 11). However, these differences would not alter our picture of the relative enthalpic stabilities of the polymorphs and are, in fact, comparable to our experimental errors. We do not consider the effect of this possible amorphous phase further.

The enthalpies of formation from the binary oxides for the cubic, trigonal, and amorphous phases of $ZrMo_2O_8$, $HfMo_2O_8$, and $ZrW_2O_8$ show the same trend: they all increase from $ZrMo_2O_8$ to $HfMo_2O_8$ and to $ZrW_2O_8$ (see Figure 1).

Thermogravimetric analysis on the amorphous $HfMo_2O_8$ sample showed a water content of about 0.9 wt %. The heat of drop solution of amorphous $HfMo_2O_8$ was corrected for the heat of evaporation of water and the heat required to raise the temperature of water from 298 to 975 K.[51] DSC of amorphous $HfMo_2O_8$ showed only exothermic peaks, probably corresponding to first the amorphous to cubic and then the cubic to trigonal phase transitions. XRD of the post-TG/DSC sample showed that the final product was the trigonal phase.

## Discussion

The enthalpies of formation from the oxides show that, among the materials in the present study, monoclinic $ZrMo_2O_8$ is the only enthalpically stable polymorph at room temperature. All other materials must be either entropically stabilized or metastable (or both, if the entropic stabilization is not sufficient to overcome the enthalpic instability). Even monoclinic $ZrMo_2O_8$ is only marginally more stable than a mixture of its binary oxides (by −5.1 ± 3.5 kJ/mol).

There is a large discrepancy between the values for $\Delta H_f$ obtained in this work and the previously reported values for trigonal $ZrMo_2O_8$, which were determined by transpiration measurements[40] and isoperibol solution calorimetry in a mixture of 10 M HF and 4.41 M $H_2O_2$.[42] Using the reported enthalpies of formation from the elements (−2577.7 to −2588.8 kJ/mol) and the enthalpies of formation for the binary oxides tabulated by Robie and Hemingway,[52] $\Delta H_f$ values for formation from the oxides of 2.4 to 13.3 kJ/mol are calculated, which are significantly less positive than ours (30−34 kJ/mol). Although the literature value obtained from transpiration measurements, 13.3 kJ/mol, is within error (±18 kJ/mol), still consistent with our data, the 2.4 ± 4.5 kJ/mol reported by Bharadwaj et al. from isoperibol solution calorimetry deviates from our results. The values determined by drop solution calorimetry have proven reliable for many refractory phases containing Zr and Hf and the same experimental approach was used for both the mixed and binary oxides. The experiments conducted by Bharadwaj assumed a complex dissolution pathway, as is evident from the eleven equations necessary to complete their thermodynamic cycle. There is no direct evidence for the formation of several species that are assumed to be present in solution, and the dissolution pathways of $ZrF_4$ and Mo metal could be different from that of $ZrMo_2O_8$. Furthermore, it is our experience that $ZrMo_2O_8$ cannot be dissolved completely in any commonly used acid, and our attempt to reproduce the experimental conditions for the isoperibol solution calorimetry (dissolution in 100 mL of 10 M HF and 4.41 M $H_2O_2$ within 5 min at room temperature) failed to give complete dissolution. Even after much longer times and additional heating, a small solid residue was observed. These problems might account for the discrepancy between the values obtained by Bharadwaj and those obtained in our work. According to our calculations, a dissolution that is only 90% complete in the reaction reported by Bharadwaj et al. would change the enthalpy of formation from the elements to be less negative by about 36 kJ/mol. This would increase the calculated $\Delta H_{f,ox}$ from 2.4 to about 38 kJ/mol, which would be close to our results. On the basis of this, we estimate that the dissolution of $ZrMo_2O_8$ in the reaction scheme of Bharadwaj et al. might have been only 90−95% complete.

Similar to $ZrMo_2O_8$, trigonal $HfMo_2O_8$ is enthalpically more stable than its cubic polymorph (the enthalpies of formation from the oxides are 46.5 ± 3.6 kJ/mol and 55.8 ± 3.1 kJ/mol, respectively). Enthalpies of formation from the elements for trigonal $HfMo_2O_8$ have previously been determined by transpiration measurements[40] and isoperibol solution calorimetry.[41] Using Robie's values for the heats of formation for the binary oxides,[52] $\Delta H_{f,ox}$ values of 2.2 to 16 kJ/mol are calculated for trigonal $HfMo_2O_8$. All of these values disagree with our results, despite the large error of

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(51) Bale, C. W.; Chartrand, P.; Degterov, S. A.; Eriksson, G.; Hack, K.; Mahfoud, R. Ben; Melancon, J.; Pelton, A. D.; Petersen, S. *Calphad* **2002**, *26*, 189.

(52) Robie, R. A.; Hemingway, B. S. *U.S. Geol. Survey Bull.* **1995**, *2131*, 461.

the transpiration measurements (±22 kJ/mol). The discrepancy between our value and that obtained by isoperibol solution calorimetry may arise from the same problems as described for $ZrMo_2O_8$. Both cubic and trigonal $HfMo_2O_8$ appear to be even less stable than the corresponding isostructural zirconium molybdate. The results for cubic and trigonal $ZrMo_2O_8$ and $HfMo_2O_8$ suggest that the formation of the cubic and trigonal phases is to a large part kinetically controlled.

The local coordination environments in the cubic and orthorhombic polymorphs of $ZrW_2O_8$ are slightly different (e.g., another tungsten−oxygen interaction develops). This presumably makes the orthorhombic phase enthalpically more stable than the cubic phase. The cubic phase is kinetically stabilized at room temperature, but the orthorhombic to cubic transformation is kinetically inhibited. Heating to ∼393 K at ambient pressure is required for back-conversion of the orthorhombic phase to the cubic material. As the cubic phase is less dense ($V_0$(orthorhombic) $\approx 0.95V_0$(cubic)), it is expected to have a higher entropy and might become more stable at higher temperatures (see the estimation of the entropy of transition later in the Discussion).

One might expect the enthalpies of formation for cubic and trigonal $ZrW_2O_8$ to be similar, as the local environments are very similar to one another, as demonstrated by EXAFS studies of both polymorphs.[10] The crystal structure of trigonal $ZrW_2O_8$ has not been solved yet, but Rietveld analysis assuming a trigonal $ZrMo_2O_8$ structure with the molybdenum exchanged for tungsten clearly indicates that the structures are closely related. However, our results show significantly different enthalpies of formation from the oxides for the cubic and the trigonal polymorphs 64.8 ± 2.8 and 49.8 ± 4.1 kJ/mol, respectively). The same is true for the molybdates, where the trigonal phase is also enthalpically more stable than the cubic, although the local molybdenum coordination environments are very similar.[2,5,11,53] This is evidence that the long-range structure (the lattice) affects stability as well as the local environment. The value of $\Delta H_{f,ox}$ for trigonal $ZrW_2O_8$ is identical within error to that of the orthorhombic polymorph (49.8 ± 4.1 and 50.6 ± 3.0 kJ/mol, respectively). Amorphous $ZrW_2O_8$ exhibits the greatest positive $\Delta H_{f,ox}$ among all phases in this study (127.8 ± 5.5 kJ/mol).

The enthalpies of formation from the oxides of cubic and orthorhombic $ZrW_2O_8$ have been estimated before by Reznitskii.[54] In this work, the enthalpies were derived from the changes in the oxygen coordination of cations upon the formation of the compounds from their binary oxides. This previous report also finds that the orthorhombic phase is more stable than the cubic one and argues that this is because the formation of the high-pressure phase from its constituent oxides is not accompanied by changes in Zr coordination number. Although the value for the enthalpies of formation from the oxides of cubic $ZrW_2O_8$ (67 ± 17 kJ/mol) agrees with our results, the one for orthorhombic $ZrW_2O_8$ (28 ± 7 kJ/mol) deviates significantly (by ∼23 kJ/mol). The difference may lie in the different approach used to derive the thermodynamic quantities, i.e., the assumption that $\Delta H_{f,ox}$ can be estimated using only the enthalpies of changes in the coordination numbers for the metals.

All the amorphous materials are less stable enthalpically than the corresponding crystalline phases at ambient pressure. This is generally the case for other materials; for example, amorphous zirconia was reported to have a 58 kJ/mol higher enthalpy than monoclinic $ZrO_2$.[55]

The possible phase transitions between the phases of the present study from the aspect of thermodynamic feasibility (enthalpic or entropic driving forces) and kinetic hindrance are summarized in Table 3. Entropies of formation could be estimated for only a few of the phases studied; therefore, it is difficult to state specifically whether an enthalpically destabilized phase is entropically stabilized or kinetically controlled. Standard molar entropies have been reported for cubic $ZrMo_2O_8$ and $ZrW_2O_8$ from heat capacity data[56] and for trigonal $ZrMo_2O_8$ and $HfMo_2O_8$ from measurements using a solid oxide galvanic cell.[45] From the standard molar entropies reported for cubic $ZrMo_2O_8$ and cubic $ZrW_2O_8$ from heat capacity measurements[56] and those of $ZrO_2$, $MoO_3$ and $WO_3$ tabulated in Robie and Hemingway,[52] the entropies of formation were estimated (using the formula $\Delta S_f = S_{m,AM_2O_8} - (S_{m,AO_2} + 2S_{m,MO_3})$, where $S_m$ is the standard molar entropy) to be 48.5 J mol$^{-1}$ K$^{-1}$ for cubic $ZrMo_2O_8$ and 55.8 J mol$^{-1}$ K$^{-1}$ for cubic $ZrW_2O_8$ at 298 K. Using our standard enthalpies ($\Delta H_{f,ox}$) and the above entropies of formation, we obtained a standard Gibbs free energy at 298 K of 30.7 kJ/mol for cubic $ZrMo_2O_8$ and 48.2 kJ/mol for cubic $ZrW_2O_8$. Assuming that $\Delta G \leq 0$ at the formation $T$, it was calculated that cubic $ZrMo_2O_8$ would be stable, relative to the binary oxides, above 931 K and $ZrW_2O_8$ would be stable above 1162 K. The latter temperature is not far from the actual synthesis temperature (1423 K) for cubic $ZrW_2O_8$.

For phases produced by solid-state reaction at a given temperature directly from the binary oxides, entropies of formation from the oxides can be estimated using the equation $\Delta S \geq \Delta H_f/T$ (from $\Delta G = \Delta H - T\Delta S$, when $\Delta G \leq 0$ at the formation $T$). Of our metastable materials, only trigonal $ZrMo_2O_8$ and $HfMo_2O_8$ and cubic $ZrW_2O_8$ can be prepared directly from the oxides by solid-state reaction, and the estimated entropies of formation are ≥33.1 (at 973 K), ≥50.8 (at 923 K), and ≥45.6 J mol$^{-1}$ K$^{-1}$ (at 1423 K), respectively. Notable is that the entropies of formation for cubic $ZrW_2O_8$ obtained by using two completely different constraints, 55.8 J mol$^{-1}$ K$^{-1}$ (from heat capacity data) and ≥45.6 J mol$^{-1}$ K$^{-1}$ (from enthalpy and formation temperature), are in reasonably good agreement.

In general, for all the crystalline polymorphs, the lower density cubic phases should have the highest entropies. This seems to be the case for the $ZrMo_2O_8$ polymorphs; the entropy of formation of the trigonal polymorph (≥33.1 J mol$^{-1}$ K$^{-1}$) calculated for 973 K is less than that of the cubic (48.5 J mol$^{-1}$ K$^{-1}$ at 298 K). The dependence of $\Delta H_f$ and

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(53) Auray, M.; Quarton, M.; Tarte, P. *Acta Crystallogr., Sect. C* **1986**, *42*, 257.

(54) Reznitskii, L. A. *Inorg. Mater.* **2002**, *38*, 1020.

(55) Molodetsky, I.; Navrotsky, A.; Paskowitz, M. J.; Leppert, V. J.; Risbud, S. H. *J. Non-Cryst. Solids* **2000**, *262*, 106.

(56) Stevens, R.; Linford, J.; Woodfield, B. F.; Boerio-Goates, J.; Lind, C.; Wilkinson, A. P.; Kowach, G. *J. Chem. Thermodyn.* **2003,** *35*, 919.

**Table 3. Summary of Possible Phase Transitions between the Phases of (a) $ZrMo_2O_8$, (b) $HfMo_2O_8$, and (c) $ZrW_2O_8$ of the Present Study with Respect to Thermodynamic Feasibility and Kinetic Control**[a]

(a) $ZrMo_2O_8$

| | trigonal | monoclinic | amorphous |
|---|---|---|---|
| cubic | C → T,<br>TD: irreversible,<br>K: slow,<br>$\Delta H_{trans} = -13.0$,<br>$\Delta V = -9.9(-8.6\%)$ | C → M,<br>TD: irreversible,<br>K: slow,<br>$\Delta H_{trans} = -50.3$,<br>$\Delta V = -28.4(-24.8\%)$ | C → A,<br>TD: feasible at P,<br>may be reversible,<br>$\Delta H_{trans} = 53.8$ |
| trigonal | | T → M,<br>TD: reversible on heating,<br>K: slow,<br>$\Delta H_{trans} = -37.3$,<br>$\Delta V = -18.5(-17.7\%)$ | T → A,<br>TD: feasible at P, may be reversible,<br>$\Delta H_{trans} = 66.7$ |
| monoclinic | | M → A,<br>TD: feasible at P may be reversible,<br>$\Delta H_{trans} = 104.1$ | |

(b) $HfMo_2O_8$

| | trigonal | amorphous |
|---|---|---|
| cubic | C → T,<br>TD: irreversible,<br>K: slow,<br>$\Delta H_{trans} = -9.3$,<br>$\Delta V = -10.2(-8.9\%)$ | C → A,<br>TD: feasible at P may be reversible,<br>$\Delta H_{trans} = 46.2$, |
| trigonal | | T → A,<br>TD: feasible at P reversible,<br>$\Delta H_{trans} = 55.5$ |

(c) $ZrW_2O_8$

| | orthorhombic | trigonal | amorphous |
|---|---|---|---|
| cubic | C → O,<br>TD: reversible on heating,<br>K: slow,<br>$\Delta H_{trans} = -14.2$,<br>$\Delta V = -6.0(-5.2\%)$ | C → T: NO,<br>TD: irreversible,<br>K: slow,<br>$\Delta H_{trans} = -15.0$,<br>$\Delta V = -17.4(-15.1\%)$ | C → A,<br>TD: feasible at P reversible,<br>$\Delta H_{trans} = 62.9$ |
| orthorhombic | | O → T: NO,<br>TD: feasible (H),<br>may be reversible,<br>K: slow,<br>$\Delta V = -11.4(-10.4\%)$ | O → A,<br>TD: feasible at P,<br>may be reversible,<br>$\Delta H_{trans} = 77.2$ |
| trigonal | | | T → A: NO,<br>TD: feasible at P,<br>may be reversible,<br>$\Delta H_{trans} = 78.0$ |

[a] Enthalpy of transition values ($\Delta H_{trans}$ in kJ/mol) were calculated from the $\Delta H_{f,ox}$ values; the accompanying volume change ($\Delta V$ in $cm^3$/mol and as %V), where available, are also shown. Nomenclature: TD, thermodynamically; K, kinetically; H, enthalpically favored; NO, not observed; C, cubic; T, trigonal; M, monoclinic; O, orthorhombic; A, amorphous. $\%V = \Delta V \times 100/V_{less\ dense\ phase}$.

$\Delta S_f$ on temperature is most likely small or negligible in the 298−1000 K range, therefore the above comparison can be safely made. The entropy of formation for the monoclinic phase is most likely even smaller than that of the trigonal phase, although as the enthalpy of formation for monoclinic $ZrMo_2O_8$ is negative, its entropy cannot be estimated using the equation $\Delta S \geq \Delta H_f/T$. A lower entropy of the monoclinic phase would suggest that a monoclinic to trigonal phase transition is feasible. Indeed, such a transition has been reported.[11,53,57] Trigonal $ZrMo_2O_8$ becomes more stable than the monoclinic phase at high temperature, above 952 K,[11] which is in agreement with the formation of the monoclinic phase at slightly lower temperature (923 K). It should be noted that the reversible trigonal to monoclinic phase transition on compression/decompression reported previously for $ZrMo_2O_8$ involves a different, lower density monoclinic polymorph.[58−60] There are no entropy data available for cubic $HfMo_2O_8$, but the cubic phase probably has a higher entropy than the trigonal, analogous to the corresponding $ZrMo_2O_8$ phases. Orthorhombic $ZrW_2O_8$ can only be obtained by the compression of the cubic phase.[4] From the known pressure of the phase transition (starting at 0.2 GPa) and the accompanying volume change (−6 $cm^3$/mol), the standard Gibbs free energy can be estimated using the equation $\Delta G^0_{298\ K} \leq P\Delta V$. Knowing the change in Gibbs free energy and the enthalpy of transition, we can estimate the entropy of transition as well as the standard entropy of formation for the orthorhombic phase. The entropy of the cubic to orthorhombic transition is calculated to be $\geq -43.6$ J $mol^{-1}$ $K^{-1}$. Thus, the estimated entropy of formation for orthor-

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(57) Serezhkin, V. N.; Efremov, V. A.; Trunov, V. K. *Russ. J. Inorg. Chem.* **1987**, *32*, 1566.

(58) Carlson, S.; Krogh Andersen, A. M. *Phys. Rev. B* **2000**, *61*, 11.

(59) Krogh Andersen, A. M.; Carlson, S. *Acta Crystallogr., Sect. B* **2001**, *57*, 20.

(60) Muthu, D. V. S.; Chen, B.; Wrobel, J. M.; Andersen, A. M. Krogh; Carlson, S.; Kruger, M. B. *Phys. Rev. B* **2002**, *65*, 064101.

**Table 4. Possible Thermodynamic Stability Fields of the Studied Polymorphs of $ZrMo_2O_8$, $HfMo_2O_8$, and $ZrW_2O_8$: Enthalpies of Formation, Entropies of Formation, and Gibbs Free Energies**

| material | $\Delta H_f$ from the oxides at 298 K (kJ/mol) | estimated $\Delta S_f$ (J mol$^{-1}$ K$^{-1}$) | estimated Gibbs free energy ($\Delta G$, kJ/mol) |
|---|---|---|---|
| cubic $ZrMo_2O_8$ | 45.2 ± 5.3 | 48.5 at 298 K | 30.7 at 298 K,<br>stable at $T > 931.1$ K |
| trigonal $ZrMo_2O_8$ | 32.2 ± 4.5 | ≥33.1 at 973 K | ≤0 at $T_f = 973$ K |
| monoclinic $ZrMo_2O_8$ | −5.1 ± 3.5 | | |
| amorphous $ZrMo_2O_8$ | 98.9 ± 5.0 | | |
| cubic $HfMo_2O_8$ | 55.8 ± 3.1 | | |
| trigonal $HfMo_2O_8$ | 46.5 ± 3.6 | ≥50.8 at 923 K | 0 at $T_f = 923$ K |
| amorphous $HfMo_2O_8$ | 102.0 ± 6.3 | | |
| cubic $ZrW_2O_8$ | 64.8 ± 2.8 | 55.8 at 298 K,<br>≥45.6 at 1423 K | 48.2 at 298 K,<br>stable at $T > 1162.5$ K,<br>≤0 at $T_f = 1423$ K |
| orthorhombic $ZrW_2O_8$ | 50.6 ± 3.0 | ≥12.2 at 298 K | ≤−1.2 at 298 K |
| trigonal $ZrW_2O_8$ | 49.8 ± 4.1 | | |
| amorphous $ZrW_2O_8$ | 127.8 ± 5.5 | | |

hombic $ZrW_2O_8$, $\Delta S_f \geq 12.2$ J mol$^{-1}$ K$^{-1}$, is significantly lower than that of the cubic phase (55.8 J mol$^{-1}$ K$^{-1}$). This is consistent with the orthorhombic to cubic phase transition being entropically favored (although kinetically controlled). Table 4 summarizes the calculated thermodynamic parameters for the phases studied.

Our results do not support the finding that the cubic phase is entropically favored relative to the amorphous phase, as was reported for $ZrW_2O_8$ by Perottoni et al.[39] Both our DSC results (exothermic recrystallization) and the drop solution enthalpies (exothermic heats of the amorphous to crystalline transition) suggest that the entropy of the amorphous phase is greater than that of the crystalline phases. We calculated the water content that could change the sign of the measured enthalpy of the amorphous to cubic phase transition in $ZrW_2O_8$ from our approximately −63 kJ/mol (calculated from the enthalpies of formation from the oxides in Table 2) to positive because of the endothermic release of water on heating and transformation. The calculation was carried out under the assumption that the water is bound only to the surface. We calculate that the presence of ~3 wt % surface water can have such a significant effect on the energetics of the phase transition, i.e., can result in endothermic recrystallization, such as the one reported by Perottoni et al.[39] It should be noted that an even smaller amount of chemically bound water (having a larger heat of vaporization than liquid water) is enough to cause the same difference. TGA on amorphous $HfMo_2O_8$ indicated that the amorphous material contained about 1% water, despite the dry starting material used for high-pressure synthesis and the product being analyzed within days after synthesis. Most of the water content of the sample was lost between 300 and 400 °C, indicating that the water was most likely chemically bound. This highlights the need for special care to ensure the dryness of the samples when studying the relative energetics of different phases by calorimetry.

High-pressure XAS studies on amorphous $ZrW_2O_8$[17] and $ZrMo_2O_8$[18] showed an increase in the average W coordination number and a slight shift in the Mo coordination. This shift from tetrahedral coordination in the cubic material toward a more centrosymmetric coordination environment of the central atom in the amorphous material was definitive for W in the tungstate. Another XAS study revealed an increase in the average Zr coordination from 6 (cubic phase) to 7 (amorphous phase) on amorphization of both $ZrW_2O_8$ and $ZrMo_2O_8$.[61] These observations mean that, on pressure-induced amorphization, the average metal coordination numbers become closer to the coordination numbers seen in the binary oxides. Thus, from a structural point of view, and in the light of Reznitskii's paper,[54] our results do not support the statement that the smaller the change in the coordination number relative to the binary oxide, the more stable the material. Thus, local coordination is clearly not the only, and may not be the dominant, factor affecting energetics.

A correlation between the enthalpies of transition ($\Delta H_{trans}$; calculated from the enthalpies of formation from the oxides) and the changes in the volume per formula unit ($\Delta V$) is noted in the crystalline to crystalline phase transitions of $ZrMo_2O_8$ (see values in Table 3). The enthalpy of transition increases as the change in volume increases. This suggests that the phase transitions that are accompanied by a greater reduction in volume are enthalpically more favored. This is not true, however, for pressure-induced amorphization, which is in all cases accompanied by an increased (more positive) enthalpy of formation, whereas the volumes per formula unit for the amorphous materials obtained by compression are expected to be smaller than those for the corresponding low-pressure crystalline polymorphs. The volume per formula unit for a recently reported high-pressure polymorph of $ZrW_2O_8$ with a cation-disordered $\alpha$-$U_3O_8$-type structure claimed to be 35% smaller than that of orthorhombic $ZrW_2O_8$; that is, its molar volume is ~71.2 cm$^3$/mol.[15] The $\Delta H_{trans}-\Delta V$ data pairs for $ZrW_2O_8$ showed no apparent correlation. As the molar volumes for the amorphous materials are not known, only one $\Delta H_{trans}-\Delta V$ data pair was available for $HfMo_2O_8$.

Considering the commonly accepted view of pressure-induced amorphization, which is that it arises due to kinetic hindrance of an equilibrium phase transition to an even higher density crystalline phase, our calorimetric data shows that the pressure-amorphized phase is indeed higher in energy (and presumably in entropy) than the low-pressure cubic form. Whether it has a true stability field or is always metastable with respect to some kinetically hindered denser crystalline polymorph, we cannot say. The pressure-amor-

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(61) Varga, T. Ph.D. Thesis, Georgia Institute of Technology, Atlanta, GA, 2005.

phized states in $AM_2O_8$ phases have also been viewed as precursors to decomposition; as reported for $ZrW_2O_8$ by Arora et al.,[62] and considered as a possibility for $ZrW_2O_8$[17] and $ZrMo_2O_8$[18] by Varga et al. In that case, the pressure-amorphized phase can be a metastable state between the low-pressure crystalline phase and a mixture of oxides with different composition.

## Conclusions

Enthalpies of formation determined for a variety of $ZrMo_2O_8$, $HfMo_2O_8$, and $ZrW_2O_8$ polymorphs using drop solution calorimetry showed that only monoclinic $ZrMo_2O_8$ is enthalpically stable with respect to the binary oxides. All other phases must be entropically stabilized and/or metastable. For $ZrMo_2O_8$, the trigonal phase is ∼37 kJ/mol less stable than the monoclinic phase, and for $ZrW_2O_8$, the orthorhombic phase was found to be more stable than the cubic phase by ∼14 kJ/mol. These results, in combination with the observed phase-transition behavior, imply that cubic $ZrW_2O_8$ is entropically stabilized relative to the orthorhombic phase and that the monoclinic to trigonal phase transition in $ZrMo_2O_8$ should be entropically favored. The pressure-amorphized phases have significantly higher enthalpies and presumably slightly higher entropies than the crystalline ones. Our results suggest that the amorphous phase can be a metastable state on a pathway to some high-pressure equilibrium phase or to decomposition.

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(62) Arora, A. K.; Sastry, V. S.; Sahu, P. C.; Mary, T. A. *J. Phys. Condens. Matter* **2004**, *16*, 1025.

(63) Achary, S. N.; Mukherjee, G. D.; Tyagi, A. K.; Godwal, B. K. *Phys. Rev. B* **2002**, *66*, 184106.

(64) Kowach, G. R. *J. Cryst. Growth* **2000**, *212*, 167

(65) Molodetsky, I.; Navrotsky, A. unpublished.

(66) Lee, T. A.; Navrotsky, A. unpublished.