

HYDROTHERMAL SYNTHESIS OF COLUMBITE-(Mn), TANTALITE-(Mn), HAFNON, AND ZIRCON AT 800–850 °C AND 200 MPa

ALYSHA G. MCNEIL, ROBERT L. LINNEN, AND ROBERTA L. FLEMMING

Department of Earth Sciences, Western University, 1151 Richmond Street North, London, ON N6A 5B7, Canada

ABSTRACT

Fully ordered columbite-(Mn), tantalite-(Mn), hafnon, and zircon were successfully synthesized using an acid solution of 6N:1N (N = normal) HF:H₂SO₄ and stoichiometric oxide mixtures. The mixtures and solutions were sealed and placed in rapid-quench cold-seal pressure vessels (CSPV) at 800–850 °C and 200 MPa. Mineral structures and compositions have been confirmed by scanning electron microscope (SEM), micro X-ray diffraction (μXRD), and electron probe microanalysis (EPMA). The unit cell parameters of the minerals determined by μXRD: Orthorhombic (*Pbcn*) columbite-(Mn) *a* 14.434(2), *b* 5.768(1), *c* 5.084(1) Å; orthorhombic (*Pbcn*) tantalite-(Mn) *a* 14.457(3), *b* 5.773(1), *c* 5.096(1) Å; tetragonal hafnon (*I4₁/amd*) *a* 6.582(2), *c* 5.9702(1) Å; and tetragonal zircon (*I4₁/amd*) *a* 6.607(4), *c* 5.9898(2) Å. The chemical formulae as determined by EPMA are very close to stoichiometric: Mn_{0.96}Nb_{2.02}O₆, Mn_{0.99}Ta_{2.01}O₆, Hf_{0.99}Si_{1.01}O₄, and Zr_{1.00}Si_{1.00}O₄, respectively.

Keywords: columbite-(Mn), tantalite-(Mn), hafnon, zircon, hydrothermal synthesis, EPMA, μXRD.

INTRODUCTION

Niobium, tantalum, hafnium, and zirconium are high field strength elements (HFSEs: high charge to ionic radius) and are usually incompatible (stay in the melt) during crystallization of major rock-forming minerals, thus concentrating in residual melts until saturation of an HFSE-bearing accessory phase (Linnen & Keppler 1997). They have become increasingly valuable in the 21st century, being used in many modern technologies such as alloys, magnets, microprocessors, *etc.*; mineral deposits that are exploited for these elements are commonly classified as rare metal or rare element deposits (Linnen *et al.* 2014). As demand for these elements increases, a better understanding of the processes that concentrate them in Earth's crust becomes essential in order to locate sufficient deposits to supply the market. These processes are commonly evaluated using experimental data, and an essential component of experimental studies is the use of endmember compositions of columbite, tantalite, hafnon, and zircon. Synthetic minerals are used because the mineralogy is consistent and controllable and eliminates interference from trace elements, and in the case of columbite–tantalite, different degrees of order that are present in natural samples (Ercit *et al.* 1995, Bartels *et al.* 2010). The synthesis of these minerals from their respective oxide equivalents requires temperatures in the range of 1000–1250 °C, which can be achieved using the flux method for hafnon and zircon, as best described by Chase & Osmer (1966), and used by Speer & Cooper (1982)

and Hanchar *et al.* (2001), and hydrothermally (in 5% HF) for columbite-(Mn) and tantalite-(Mn), as demonstrated by Linnen & Keppler (1997) and Fiege *et al.* (2011), who successfully synthesized columbite-(Mn) and tantalite-(Mn). Columbite-(Mn) was synthesized at 800 °C using this method, however, for tantalite-(Mn) temperatures of 1000 and 1250 °C, respectively, were required, which is outside the range of temperatures attainable in a normal cold-seal pressure vessel (CSPV). Hafnon and zircon have also been synthesized hydrothermally using gelatinous ZrO₂ and SiO₂ between 150 and 700 °C, as presented by Frondel & Collette (1957), with samples synthesized between 150 and 350 °C requiring extra heating to remove substituted hydroxyl groups. Lei *et al.* (2014) hydrothermally synthesized columbite-(Mn) ellipsoids by adding an MnCl₂ solution to a potassium polyoxoniobate (K₇HNb₆O₁₉ · 13H₂O) solution under continuous magnetic stirring and heating the resulting precipitate to 150 °C for 24 hours. It is preferred not to use alkali elements in columbite and tantalite synthesis experiments because of the possibility of crystallizing minerals such as lueshite (NaNbO₃) or compounds such as KNbO₃ or LiNbO₃ and their tantalum equivalents (Goh *et al.* 2003). Columbite-(Mn) can also be synthesized by non-aqueous methods as described by Zhang *et al.* (2008) and Hu *et al.* (2012) at temperatures around 200 °C. These three methods, while synthesizing columbite at low temperature, only produce nano-scale crystals. Nanocrystals are not preferred for dissolution

TABLE 1. SUMMARY OF EXPERIMENT PROPERTIES

Experiment Name	MnNb ₂ O ₆ Syn1	MnNb ₂ O ₆ Syn2	MnTa ₂ O ₆ Syn1	MnTa ₂ O ₆ Syn2	HfSiO ₄ Syn1	ZrSiO ₄ Syn1
Oxide mixture (mg)	351.4	301.2	204.3	154.0	149.6	151.2
Acid mixture (mg)	50.4	100.6	105.4	97.6	104.5	74.6
Oxide to Acid ratio	7:1	3:1	2:1	1.5:1	1.5:1	2:1
Temperature (°C)	800	800	400	850	850	850
Pressure (MPa)	200	200	200	200	200	200
Duration (days)	5	9	4	5	11	11
Successful?	Yes	Yes	No	Yes	Yes	Yes

and partition experiments because crystal-free regions of glasses need to be analyzed after the experiments are quenched.

The method described herein is relatively simple and allows for the synthesis of hafnion, zircon, columbite-(Mn), and tantalite-(Mn) at 800–850 °C in CSPVs, eliminating the need for the use of multiple different synthesis methods for individual minerals. This technique

also allows for lower temperature synthesis of tantalite-(Mn) than previously described. Successful synthesis was achieved using a technique from hydrometallurgy, which for years has used acid mixtures to dissolve columbite and tantalite for ore processing (*e.g.*, Nishimura *et al.* 1964, Ayanda & Adekola 2011). Dissolution of stoichiometric oxide mixtures and crystallization into their respective minerals at low

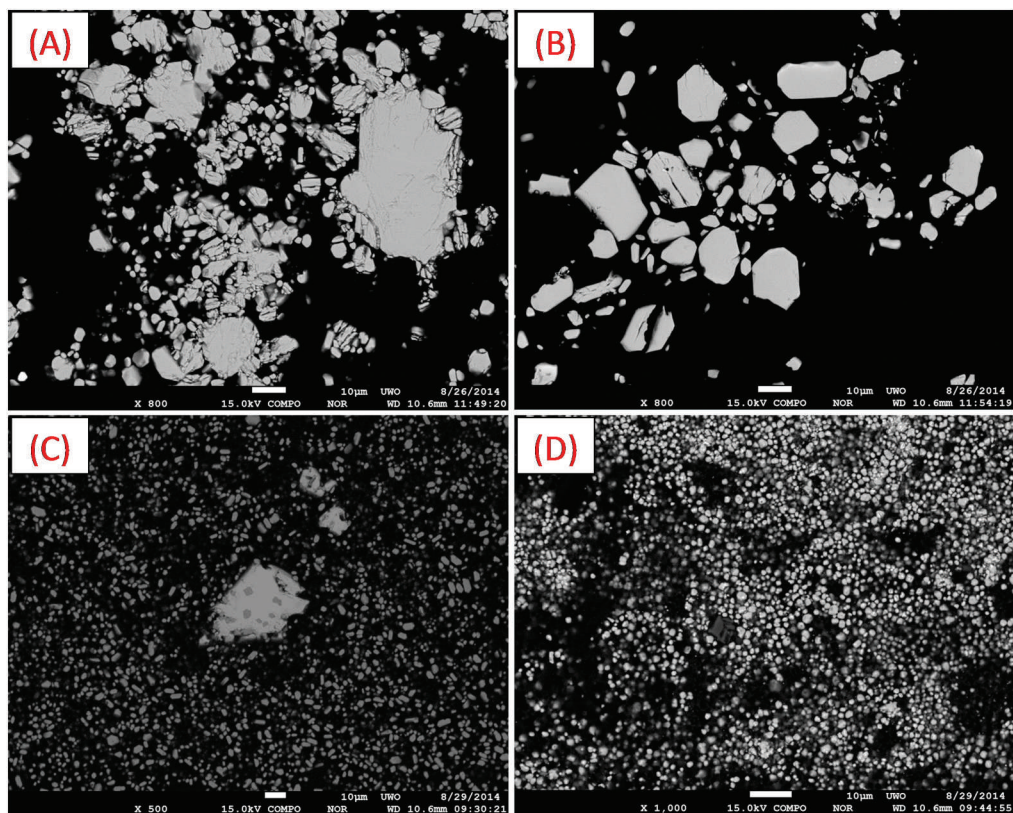


FIG. 1. SEM image of: (A) MnNb₂O₆ Syn1 crystals (light gray) in epoxy (black); (B) MnTa₂O₆ Syn2 crystals (light gray) in epoxy (black); (C) HfSiO₄ Syn1 crystals (small mid-gray specks) with residual HfO₂ surrounding HfSiO₄ (large light gray around mid-gray) in epoxy (black), dark gray crystals are hafnion crystals just below the surface of the epoxy; (D) ZrSiO₄ Syn1 crystals (light gray) in epoxy (black), dark gray crystals are zircons just below the surface of the epoxy. For all images, the white scale bar is 10 μm.

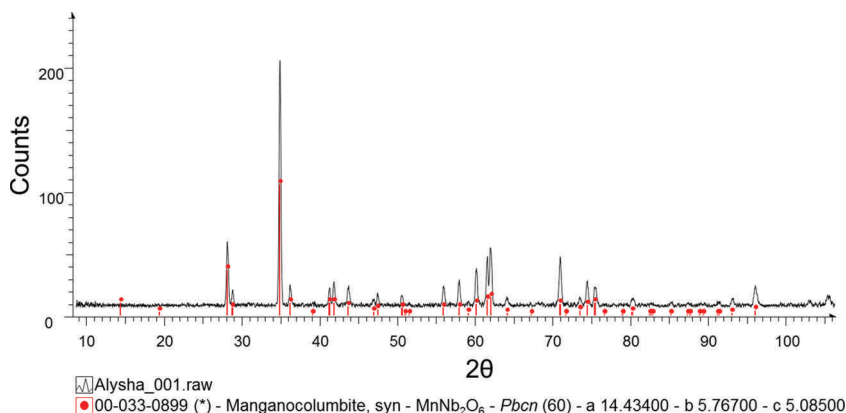


FIG. 2. MnNb_2O_6 Syn1 X-ray diffraction pattern.

temperature should also be possible with the correct acid ratio. The ratio of 6N:1N (N = normal) $\text{HF}:\text{H}_2\text{SO}_4$ was utilized because Htwe & Lwin (2008) determined that columbite and tantalite are highly soluble in this mixture. As Nb, Ta, and Hf and Zr have similar chemical properties, additional experiments were conducted using stoichiometric mixtures of HfO_2 , ZrO_2 , and SiO_2 to determine if synthesis of hafnon and zircon from these mixtures is also possible.

EXPERIMENTAL PROCEDURE

Large amounts (between 7 and 19 g) of stoichiometric oxide mixtures of the desired minerals were first made to reduce weighing errors. The pure oxide components were

all purchased from Alfa Aesar with purities of: Ta_2O_5 – 99.85%, Nb_2O_5 – 99.5%, MnO – 99%, HfO_2 – 99.95%, ZrO_2 – 99.978%, and SiO_2 – 99.5%. Powders were then placed in a drying oven at 110 °C for 20 min to drive off excess water. Columbite-(Mn) (MnNb_2O_6), tantalite-(Mn) (MnTa_2O_6), hafnon (HfSiO_4), and zircon (ZrSiO_4) were then synthesized by combining stoichiometric oxide mixtures and varying amounts of a 6N:1N $\text{HF}:\text{H}_2\text{SO}_4$ solution, then sealing them in Au capsules (length 30, i.d. 4.8, o.d. 5.0 mm), and placing the capsules in rapid quench CSPVs at 800–850 °C and 200 MPa for 4 to 11 days. The oxide to acid weight ratios were varied to determine the effect on crystal size and experiment success. The larger the oxide to acid ratio, the larger the crystal yield per experiment, which shows that relatively large volumes will

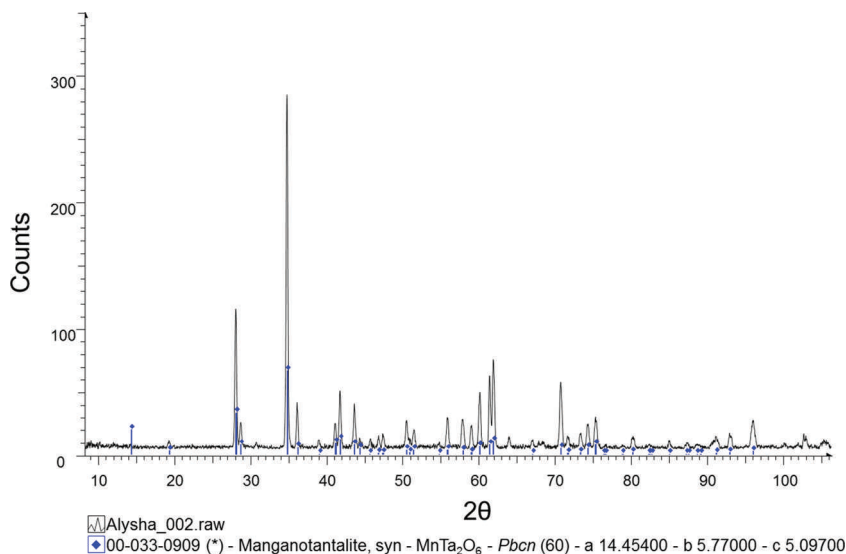


FIG. 3. MnTa_2O_6 Syn2 X-ray diffraction pattern.

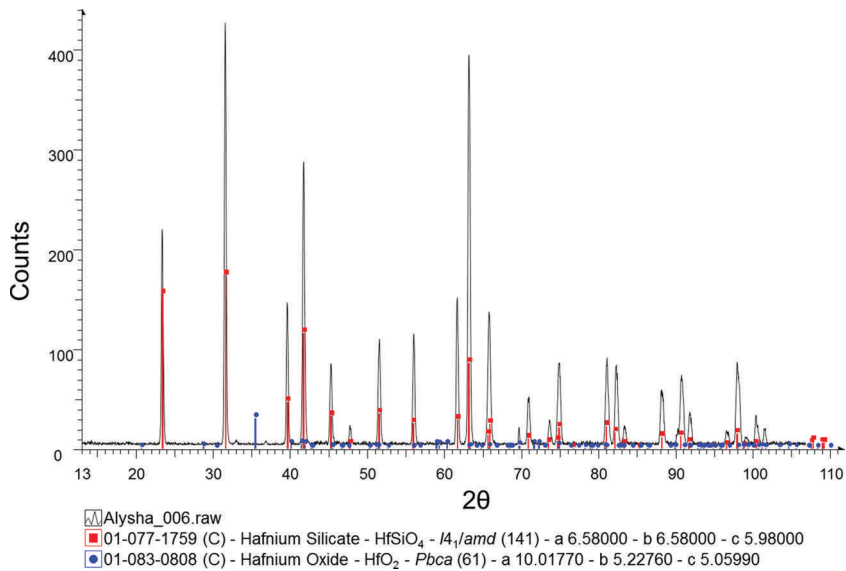


FIG. 4. HfSiO₄ Syn1 X-ray diffraction pattern.

react completely. The amounts of oxide mixture, acid, temperature, and time used for each experiment are summarized in Table 1. The capsules were opened and the contents were washed with distilled water on Pyrex® dishes and then dried in an oven to remove any excess acid remaining. The contents were then carefully recovered and analyzed by micro X-ray diffraction (μXRD), scanning electron microscope (SEM), and electron probe micro-analysis (EPMA).

Micro X-ray Diffraction

The crystals were analyzed by μXRD using a Bruker D8 Discover microdiffractometer in the Department of Earth Sciences at Western University (see Flemming 2007) with a CoKα X-ray source (λ = 1.78897 Å) at 35 kV and 45 mA. For the columbite-(Mn), tantalite-(Mn), and hafnion crystals, the beam was collimated using a 300 μm monocapillary with a 100 μm insert. For the zircon crystals, a Göbel mirror parallel optics system was used with a 300 μm pinhole snout in place of the monocapillary. The theta-theta instrument allowed samples to remain stationary and horizontal while the source and detector

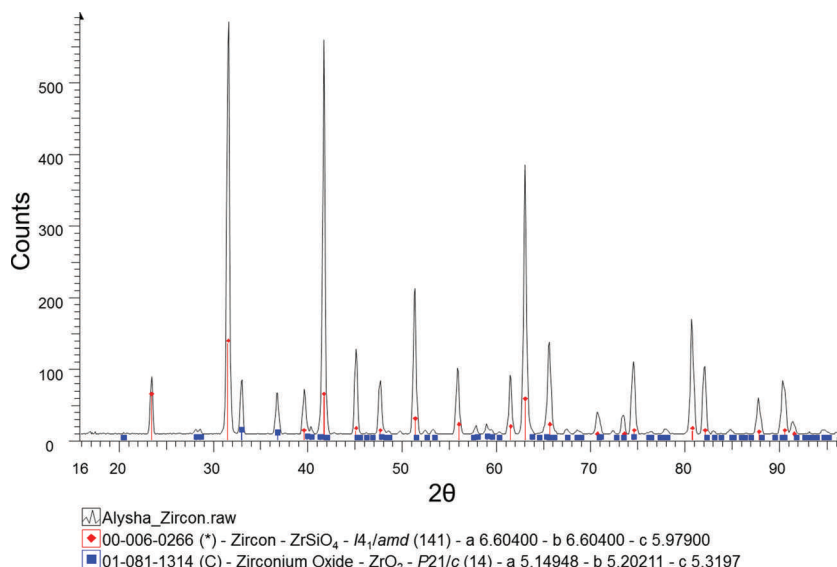
were set to the desired θ₁ + θ₂ = 2θ, where θ₁ = θ₂ in coupled scan mode. Coupled scans were used to collect the data, which were then processed from General Area Detector Diffraction System (GADDS) images using DIFFRAC PLUS Evaluation software (EVA). Unit-cell parameters, (Table 2) were determined with CELREF (Laugier & Bochu 2003) using starting unit-cell parameters from best-matching phases in EVA from the International Centre for Diffraction Data Powder-Diffraction File (ICDD PDF4 + 2010) database.

Electron Probe Micro-analysis

Electron probe micro-analyses were completed at the Earth and Planetary Materials Analysis Laboratory at Western University, using a JEOL JXA-8530F field-emission electron microprobe using WDS detectors. Probe conditions were 15 kV accelerating voltage and 20 nA current with a beam size of ~1 μm. Mineral calibration standards used for analyses were pure tantalum wire for Ta (99.996%, Alfa Aesar, USA); pure manganese for Mn (99.99%, Johnson Matthey Chemicals, UK); pure niobium wire for Nb (99.96, Alfa Aesar, USA); pure zirconium

TABLE 2. REFINED UNIT CELL PARAMETERS OF SUCCESSFUL EXPERIMENTS

Experiment Name	MnNb ₂ O ₆ Syn1	MnNb ₂ O ₆ Syn2	MnTa ₂ O ₆ Syn2	HfSiO ₄ Syn1	ZrSiO ₄ Syn1
<i>a</i> (Å)	14.434 (±0.002)	14.435 (±0.004)	14.457 (±0.003)	6.582 (±0.001)	6.607 (±0.004)
<i>b</i> (Å)	5.768 (±0.001)	5.766 (±0.001)	5.773 (±0.001)	6.582 (±0.001)	6.607 (±0.004)
<i>c</i> (Å)	5.084 (±0.001)	5.085 (±0.001)	5.096 (±0.001)	5.970 (±0.0001)	5.9898 (±0.0002)
Volume (Å ³)	423.3	423.2	425.4	258.6	261.5
Space group	<i>Pbcn</i>	<i>Pbcn</i>	<i>Pbcn</i>	<i>I4₁/amd</i>	<i>I4₁/amd</i>

FIG. 5. $ZrSiO_4$ Syn1 X-ray diffraction pattern.

wire for Zr (99.7%, Alfa Aesar, USA); quartz for Si in zircon; and synthetic hafnon for Si and Hf in hafnon. Errors on analyses were no larger than ± 0.78 wt.% on Nb and Ta, ± 0.22 wt.% on Mn, ± 0.80 wt.% on Zr and Hf, and ± 0.87 wt.% on Si (refer to Table 3 for detailed analyses and errors). Scanning electron microscope images were taken using the SEM on the microprobe.

RESULTS

The $MnTa_2O_6$ Syn1 experiment was attempted at low temperature (400 °C, 200 MPa, and 4 days) to determine if high temperature was necessary for the

reaction to occur. The experiment was not successful, as the oxides did not react to form tantalite-(Mn). Subsequent experiments were conducted at temperatures of 800 and 850 °C, which successfully produced crystals ranging in size from <1 to 250 μm . The columbite-(Mn) experiments produced crystal sizes throughout the entire size range (up to 250 μm), and the tantalite-(Mn), hafnon, and zircon experiments produced crystals up to 20 μm in size. The change in acid to powder ratio had no effect on grain size. In the columbite-(Mn) and tantalite-(Mn) experiments, the synthesized mineral phase was the only phase identified. In the hafnon and zircon experiments, small amounts of

TABLE 3. AVERAGE OF EPMA RESULTS FROM SUCCESSFUL EXPERIMENTS

Experiment Name	$MnNb_2O_6$ Syn1	$MnNb_2O_6$ Syn2	$MnTa_2O_6$ Syn2	$HfSiO_4$ Syn1	$ZrSiO_4$ Syn1
MnO (wt.%)	20.24 (± 0.16)	20.20 (± 0.22)	13.52 (± 0.21)		
Nb_2O_5 (wt.%)	80.10 (± 0.70)	79.80 (± 0.78)			
Ta_2O_5 (wt.%)			85.77 (± 0.68)		
SiO_2 (wt.%)				22.65 (± 0.87)	32.78 (± 0.63)
HfO_2 (wt.%)				77.50 (± 0.80)	
ZrO_2 (wt.%)					67.45 (± 0.67)
Total	100.34	100.00	99.28	100.15	100.23
Chemical formula*	$Mn_{0.96}Nb_{2.02}O_6$	$Mn_{0.96}Nb_{2.02}O_6$	$Mn_{0.99}Ta_{2.01}O_6$	$Hf_{0.99}Si_{1.01}O_4$	$Zr_{1.00}Si_{1.00}O_4$
n^{**}	10	10	10	10	4

Errors are $\pm 1\sigma$

*All chemical formulae have errors ± 0.01

** n = Number of spots analyzed to determine average value reported and standard deviation (σ). More spots could be analyzed on experiments that produced larger crystals.

TABLE 4. μ XRD DATA FROM COLUMBITE-(Mn) EXPERIMENTS

MnNb ₂ O ₆ Syn1						MnNb ₂ O ₆ Syn2					
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>l</i> / <i>l</i> ₀ (%)	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>l</i> / <i>l</i> ₀ (%)
3	1	0	3.6939	3.6946	26.6	3	1	0	3.6963	3.6942	23.1
4	0	0	3.6099	3.6083	7.1	3	1	1	2.9860	2.9887	100.0
3	1	1	2.9913	2.9888	100.0	0	2	0	2.8805	2.8827	12.6
0	2	0	2.8846	2.8840	9.2	0	0	2	2.5429	2.5423	21.4
0	0	2	2.5427	2.5422	8.0	0	2	1	2.5062	2.5077	21.8
0	2	1	2.5088	2.5085	10.5	6	0	0	2.4083	2.4058	8.9
6	0	0	2.4067	2.4056	8.7	3	0	2	2.2485	2.2479	7.6
3	2	1	2.2247	2.2243	5.9	3	2	1	2.2248	2.2238	10.0
3	1	2	2.0946	2.0943	4.9	3	1	2	2.0938	2.0943	10.9
5	0	2	1.9076	1.9078	8.7	1	3	0	1.9058	1.9050	7.8
6	2	0	1.8475	1.8473	11.2	6	2	0	1.8478	1.8471	5.6
3	3	0	1.7852	1.7854	15.8	7	1	1	1.8133	1.8139	1.8
6	0	2	1.7483	1.7473	20.6	1	3	1	1.7821	1.7839	9.7
6	2	1	1.7370	1.7362	23.8	6	0	2	1.7472	1.7475	11.9
4	2	2	1.6861	1.6861	4.3	6	2	1	1.7351	1.7361	14.8
3	1	3	1.5411	1.5405	20.5	4	2	2	1.6857	1.6859	2.8
6	2	2	1.4948	1.4944	3.6	3	1	3	1.5394	1.5405	15.3
9	1	1	1.4787	1.4783	10.8	6	2	2	1.4958	1.4943	5.6
0	2	3	1.4616	1.4612	8.0	0	2	3	1.4614	1.4611	16.2
0	4	1	1.3870	1.3873	3.8	0	4	0	1.4418	1.4414	1.2
9	3	0	1.2313	1.2315	3.7	0	4	1	1.3873	1.3867	3.8
12	0	0	1.2024	1.2028	8.9	9	1	2	1.3202	1.3205	2.5
9	1	3	1.1421	1.1418	2.4	6	3	2	1.2919	1.2929	1.2
6	0	4	1.1233	1.1239	3.4	10	2	1	1.2513	1.2510	2.3
						9	3	0	1.2314	1.2314	5.0
						3	1	4	1.2023	1.2020	4.7

unreacted HfO₂ and ZrO₂ were present along with hafnon and zircon, respectively. Figure 1 shows SEM images of portions of the samples held within Crystal-bondTM and polished for EPMA analyses. Fully ordered columbite and tantalite were the only phases identifiable from powder diffraction data of the columbite-(Mn) and tantalite-(Mn) experiments (Figs. 2 and 3) and determined using the formula for order as described in Ercit *et al.* (1995); percent order = $1727 - 941.6(c - 0.2329a)$. Based on the above formula, the order in the samples ranges from 99 to 105% of the Ercit *et al.* (1995) values. In the hafnon and zircon synthesis experiments, some diffraction peaks matched HfO₂ and ZrO₂ in addition to HfSiO₄ and ZrSiO₄ (Figs. 4 and 5), showing that a small amount of unreacted hafnium oxide and zirconium oxide, respectively, remained in the samples. The unit-cell parameters for the samples are summarized in Table 2 and EPMA results are summarized in Table 3. Detailed diffraction data for all experiments are presented in Tables 4–6. Mineral stoichiometries were calculated using a fixed oxygen value of 6 for columbite-(Mn) and tantalite-(Mn), and 4 for hafnon and zircon. If

stoichiometries are calculated using cations rather than fixed oxygen, the zircon, hafnon, and tantalite-(Mn) formulae are identical within error, and columbite-(Mn) is Mn_{0.96}Nb_{2.04}O_{6.05} for both experiments. Tables 4–6 contain the μ XRD data and refined *d*-spacings for all of the successful experiments.

DISCUSSION

MnNb₂O₆ Syn1 and MnNb₂O₆ Syn2 have nearly identical unit-cell parameters. This is important to note because MnNb₂O₆ Syn1 had an approximately 7:1 oxide mixture to acid ratio and ran for 5 days, whereas MnNb₂O₆ Syn2 had a 3:1 ratio and ran for 9 days. The former experiment shows that columbite can be synthesized with a low oxide mixture/acid ratio, and a shorter amount of time, with an increased amount of crystals synthesized per experiment. MnTa₂O₆ Syn2 was completed with a 1.5:1 oxide mixture to acid ratio, because tantalite-(Mn) was more difficult to synthesize than columbite-(Mn). The chemical formulae determined from

TABLE 5. μ XRD DATA FROM TANTALITE-(Mn) EXPERIMENTS

MnTa ₂ O ₆ Syn2					
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> / <i>I</i> ₀ (%)
1	1	0	5.3731	5.3614	2.4
3	1	0	3.7032	3.6994	39.5
4	0	0	3.6206	3.6142	7.5
2	1	1	3.3811	3.3778	1.9
3	1	1	2.9994	2.9938	100.0
0	2	0	2.8908	2.8865	13.1
2	2	0	2.6863	2.6807	2.5
0	0	2	2.5513	2.5482	7.3
0	2	1	2.5141	2.5116	16.4
6	0	0	2.4094	2.4094	12.8
2	2	1	2.3730	2.3725	3.1
5	1	1	2.3053	2.3056	2.8
3	0	2	2.2537	2.2526	3.8
3	2	1	2.2271	2.2273	4.1
3	1	2	2.0992	2.0985	8.1
4	2	1	2.0611	2.0625	5.4
7	1	0	1.9455	1.9446	2.0
0	2	2	1.9102	1.9103	8.6
6	2	0	1.8501	1.8497	8.3
7	1	1	1.8168	1.8168	6.7
1	3	1	1.7862	1.7865	16.0
6	0	2	1.7522	1.7507	20.7
6	2	1	1.7396	1.7387	25.2
4	2	2	1.6889	1.6889	3.5
4	2	2	1.6887	1.6889	3.5
1	1	3	1.6198	1.6194	2.2
7	1	2	1.5451	1.5459	18.9
5	3	1	1.5279	1.5282	3.7
6	2	2	1.4970	1.4969	4.5
9	1	1	1.4810	1.4807	6.7
3	3	2	1.4635	1.4631	9.0
6	3	1	1.4415	1.4422	1.0
7	3	0	1.4072	1.4079	1.1
0	4	1	1.3884	1.3886	2.9
7	3	1	1.3577	1.3571	1.3
9	1	2	1.3232	1.3227	2.2
6	3	2	1.2945	1.2950	1.6
7	1	3	1.2788	1.2793	1.3
5	4	1	1.2519	1.2518	3.6
7	3	2	1.2322	1.2323	3.5
6	4	1	1.2029	1.2031	8.1
9	1	3	1.1436	1.1440	2.8

EPMA analysis of the columbite-(Mn) and tantalite-(Mn) are Mn_{0.96}Nb_{2.02}O₆ and Mn_{0.99}Ta_{2.01}O₆, respectively. The synthesis was successful because both the identifiable phases from the diffraction patterns and the chemical

formulae as determined by EPMA matched columbite-(Mn) and tantalite-(Mn), respectively. As mentioned above, in the case of hafnon and zircon, some diffraction peaks match HfO₂ and ZrO₂ in addition to HfSiO₄ and ZrSiO₄. Therefore, small amounts of unreacted hafnium oxide and zirconium oxide remained in the sample. Since no SiO₂ was identified, this could be attributed to the starting mixture having a slight excess of HfO₂. Another possibility is that the HF dissolved SiO₂, creating SiF₄ or other Si-F species present in solution, reducing the amount of SiO₂ available to react with the other oxides. This is supported by SEM images of the hafnon and zircon crystals (Fig. 1). The chemical formulae for the synthesized hafnon and zircon are Hf_{0.99}Si_{1.01}O₄ and Zr_{1.00}Si_{1.00}O₄, respectively, with no extra HfO₂ or ZrO₂ present in the analyzed crystals. This demonstrates that hydrothermal synthesis of hafnon, zircon, columbite-(Mn), and tantalite-(Mn) is successful at 800–850 °C, 200 MPa, in a 6N:1N HF:H₂SO₄ solution.

APPLICATIONS

The successful synthesis of columbite-(Mn), tantalite-(Mn), zircon, and hafnon at temperatures attainable by CSPVs is essential to the experimental study of these minerals and the natural environments in which they form. Columbite, tantalite, and zircon are commonly associated with evolved granites and pegmatites, as well as carbonatites, with the former being the subject of experimental studies in an attempt to determine crystallization mechanisms. Synthetic columbite-(Mn), tantalite-(Mn), hafnon, and zircon can be used in solubility experiments to determine the solubility of Nb, Ta, Hf, and Zr in highly fluxed granitic melts and pegmatites of varying compositions. The method described herein provides a simple means of synthesis of these minerals for use in experimental studies. Some examples of these types of experiments are Bartels *et al.* (2010), Chevychelov *et al.* (2010), Van Lichtervelde *et al.* (2010), Fiege *et al.* (2011), and Aseri *et al.* (2014). To date, experimental studies have used synthetic endmember compositions as starting materials. Our method can potentially be used to synthesize compositions along the columbite–tantalite and zircon–hafnon solid solutions. Solubility experiments are usually performed at 800 °C or greater, which is higher than the start of pegmatite crystallization, at approximately 700 °C, because at low temperatures other minerals also crystallize (most commonly micas); crystallization of other minerals makes it impossible to calculate solubility product constants. Therefore, experiments are performed at higher temperatures and the data is extrapolated to the zone in which pegmatites typically crystallize. Zircon and hafnon are important starting materials for future experimental studies; this is because Van Lichtervelde *et al.* (2007) showed that at the Tanco pegmatite, MB, Canada, zircon and Ta oxides crystallized from the same melt at the same time, showing that similar mechanisms cause zircon/hafnon and Nb/Ta oxides to crystallize.

TABLE 6. μ XRD DATA FROM HAFNON AND ZIRCON EXPERIMENTS

HfSiO ₄ Syn1						ZrSiO ₄ Syn1					
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> / <i>I</i> _o (%)	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> / <i>I</i> _o (%)
0	1	1	4.4311	4.4219	51.1	0	1	1	4.4319	4.4376	13.9
0	2	0	3.2964	3.2910	100.0	0	2	0	3.3056	3.3036	100.0
1	2	1	2.6439	2.6401	33.7	1	2	1	2.6466	2.6499	10.8
2	2	0	2.3262	2.3271	19.2	1	1	2	2.5192	2.5213	95.6
0	2	2	2.2116	2.2109	4.6	2	2	0	2.3365	2.3360	20.6
0	3	1	2.0586	2.0593	25.1	0	3	1	2.0703	2.0671	35.3
1	0	3	1.9055	1.9048	26.2	1	0	3	1.9112	1.9112	16.0
2	3	1	1.7460	1.7457	34.9	2	3	1	1.7517	1.7523	14.3
3	1	2	1.7079	1.7073	92.4	3	1	2	1.7133	1.7136	65.3
2	1	3	1.6471	1.6486	31.5	2	1	3	1.6536	1.6543	22.3
1	4	1	1.5419	1.5422	11.2	0	3	3	1.4787	1.4792	17.6
0	0	4	1.4924	1.4924	6.0	3	3	2	1.3821	1.3817	27.9
3	3	2	1.3760	1.3766	20.7	0	2	4	1.3639	1.3639	16.4
0	2	4	1.3595	1.3592	18.6	2	2	4	1.2612	1.2606	13.1
3	2	3	1.3447	1.3452	4.6						
0	5	1	1.2852	1.2855	13.1						
2	2	4	1.2563	1.2563	16.5						
1	4	3	1.2448	1.2452	7.9						
5	2	1	1.1977	1.1974	3.5						
5	1	2	1.1848	1.1848	19.6						
0	1	5	1.1750	1.1748	1.8						
4	4	0	1.1636	1.1636	7.1						

Another application to geological environments is to investigate the cause of cation order-disorder in the crystal structures of columbite and tantalite. In nature, columbite and tantalite are commonly found to have a cation-disordered crystal structure, whereas their synthetic equivalents have a cation-ordered crystal structure. The disordered structure was first described by Nickel *et al.* (1963) but has since been characterized by Wise *et al.* (1985) and Ercit *et al.* (1995). This new method of synthesis at temperatures attainable by CSPVs for both tantalite-(Mn) and columbite-(Mn) has allowed for the study of mechanisms that may cause disorder, such as trace elements and undercooling, using the same synthesis method and at temperatures and conditions more comparable to nature. These parameters are currently being investigated in a study by the authors.

CONCLUSION

Columbite, tantalite, hafnon, and zircon are minerals commonly used in experimental petrology to study HFSE mineralization in pegmatites and other types of ore deposits. In order to perform accurate experiments, synthetic equivalents of these minerals are used to eliminate the effect of trace elements and variable structural states inherent in natural samples. These types of minerals have

been used in mineral solubility experiments of pegmatites and granites, and experiments of cation order-disorder of columbite-(Mn) and tantalite-(Mn). Previous synthesis required different methods depending on the mineral in question, or as in the case of tantalite-(Mn), temperatures greater than 1000 °C. This method was adopted from hydrometallurgy literature. A 6N:1N HF:H₂SO₄ solution resulted in the successful synthesis of columbite-(Mn), tantalite-(Mn), hafnon, and zircon at 800–850 °C and 200 MPa. This provides an alternative method for synthesizing all of these minerals, with grain sizes up to 250 μ m for columbite-(Mn), and up to 20 μ m for tantalite-(Mn), zircon, and hafnon, using the same method in rapid quench CSPVs, as opposed to multiple different techniques that require higher temperatures or produce sub- μ m grains.

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