

**Interim Report on Task 1.2: Near Equilibrium Processing  
Requirements**

**Part 1 of 2**

**To Lawrence Livermore National Laboratory for Contract  
B345772**

M W A Stewart, E R Vance R A Day and A Brownscombe

April 5, 1999

*U.S. Department of Energy*

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**Stewart, Vance, Day  
Brownscombe**

APPROVED BY

**E R Vance**

Australian Nuclear Science and Technology Organisation  
Postal Address: Private Mail Bag 1, Menai, NSW 2234, Australia  
Materials Division: Telephone +61 2 9717 3265 • Facsimile +61 2 9543 7179

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## 1 SUMMARY

The following ceramics were prepared for this study: the baseline ceramic, the baseline ceramic plus process impurities, a zirconolite-rich composition, a brannerite-rich composition, a composition designed to have ~ 10 % perovskite in addition to the normal baseline phases, and an ~ 10 % phosphate-doped batch. These samples were prepared by oxide (via wet or dry milling) and alkoxide-routes.

The milling method has a direct effect on the samples. Incomplete milling leads to inhomogeneity in the microstructure. The main effect of incomplete milling is that unreacted actinide oxides remain in the microstructure, usually surrounded by brannerite. The phase composition also alters due to the actinide being tied up in the unreacted oxide, e.g., the pyrochlore has less actinide and additional phases, such as zirconolite may form.

The approach to equilibrium is determined by a number of factors - the efficiency of the milling, the sintering time, the sintering temperature and the batch composition. The latter is very important, e.g., the zirconolite-rich batch has a slower approach to equilibrium than the baseline ceramic requiring higher sintering temperatures or longer sintering times. The addition of process impurities dramatically alters the approach to equilibrium. The additives produce a silicate liquid phase (at the sintering temperatures), which aids the dissolution and diffusion of the actinide oxide and densification such that even the relatively inhomogeneous dry milled oxide-route samples reach 90 – 95 % of their equilibrium state on sintering at 1350°C for 4 hours.

In terms of approach to equilibrium, the following summarises the results. For 4 h at 1350°C samples: dry-milled oxide samples reach ~ 50 – 80 % of their equilibrium state, except for the baseline + additives batch which achieves ~ 90 - 95 % equilibrium. The wet-milled oxide route samples reach ~ 90 – 100 % equilibrium and alkoxide-route samples reach ~ 95 – 100 % equilibrium. The following refers to alkoxide or wet-milled oxide-routes. Sintering for 75 hours at 1350°C gives ~ 98 – 100 % equilibrium. Sintering at 1300°C gives ~ 80 – 95 % equilibrium. Sintering at 1400°C is more difficult to judge as the phase chemistry can change, but generally, the samples sintered for 4 hours at 1400°C are similar to the samples sintered for 75 hours at 1350°C.

Generally, the compositions formed the phases expected. The exception was the batch with nominally ~ 10 % perovskite, which did not contain perovskite (except for the poorly milled Th/U-doped batch and in this case it was due to the Th being retained in large ThO<sub>2</sub> grains). The following apply to the 16 hour wet-milled oxide-route and alkoxide-route batches sintered at 1350°C for 4 hours.

- The baseline ceramics formed pyrochlore with 10 – 20 vol. % brannerite and 3 – 5 vol. % Hf-doped rutile.
- The baseline + impurities ceramics formed pyrochlore with ~ 15 vol % 2M zirconolite, 10 – 20 brannerite, 2 - 3 vol. % Hf-doped rutile and ~ 1 - 2 vol. % of an intergranular silicate phase, probably a glass. The impurities lead to grain growth – probably via liquid phase sintering in the samples. The samples warped when sintered at 1350°C and above. The additives reduced the effect of the green processing, the dry milled oxide-route had no unreacted actinide oxide, and even the sample sintered at 1300°C for 4 hours only contained a trace of unreacted ThO<sub>2</sub>.

- The zirconolite-rich ceramics formed an approximately equal mixture of zirconolite and pyrochlore with ~ 15 – 20 vol. % brannerite and sometimes a little (< 5 vol. %) Hf-doped rutile.
- The brannerite-rich samples consisted of an approximately equal mixture of brannerite and pyrochlore and sometimes ~ 2 – 3 vol. % Hf-doped rutile was present.
- The nominally ~ 10 % perovskite samples had no perovskite. The additional Ca formed pyrochlore with Ca content in the Ca site being close to unity. The additional phases formed depend on whether the sample was Th or Pu-doped. For Th-doped batches, 5 - 20 vol. % brannerite and 5 – 10 vol. % Hf-doped rutile were present. In the Pu-doped samples only ~ 5 vol. % rutile was present.
- The phosphate-doped samples typically consisted of pyrochlore with 15 - 20 vol. % brannerite, 5 – 10 vol. % whitlockite and 3 – 7 vol. % Hf-doped rutile. The whitlockite, nominally,  $\text{Ca}_3(\text{PO}_4)_2$  contains Gd, Hf, U, Th and Ti.

The results of the Pu/U-doped samples are similar to those for Th/U-doped samples. The Th/U-doped samples had similar phase compositions to the Pu/U-doped samples, which indicate that Th is a good surrogate for Pu in the phase assemblages studied. The major exception was that the Th has a greater tendency to form brannerite and hence, the Th-doped ceramics tend to have slightly more brannerite. The Pu, U and Th partition as expected – mainly into the pyrochlore, brannerite and zirconolite. Some also entered the whitlockite. The amounts in the minor phases, rutile, glass and whitlockite, are small and the neutron absorbers Hf and Gd can also be found in these phases.

## 2 INTRODUCTION

### 2.1 Goal of Task 1.2

The purpose of these tests is to compare the products obtained by plant-like fabrication processes to the products under near equilibrium conditions.

### 2.2 Strategy Adopted

Several variables were examined in this study – composition, preparation route (see below), milling time, sintering time, sintering temperature and sintering atmosphere. The aim was to produce a variety of powder batches ranging from homogeneous (wet ball milled) to heterogeneous (dry ball milled) and examine how they approached equilibrium under a variety of sintering conditions.

The compositions of the samples tested were:

- the baseline ceramic
- the baseline ceramic plus process impurities
- a zirconolite-rich composition
- a brannerite-rich composition
- a composition designed to have ~ 10 % perovskite (note, that this batch did not actually produce perovskite in either, Ar or air sintering atmospheres)
- an ~ 10 % phosphate-doped batch.

Details of the compositions can be found in the Experimental section below.

Th was used as a surrogate for Pu. It avoids some of the redox problems encountered if Ce is used and is believed to be a closer analog of Pu.

Th/U-doped batches of powder were prepared by three methods:

- Alkoxide-route wet ball milled
- Oxide-route wet ball milled
- Oxide-route dry ball milled

The alkoxide-route method uses alkoxides and nitrates as the raw materials. This route should produce homogeneous mixtures and pellets. The oxide-route uses oxides plus  $\text{Ca}(\text{OH})_2$  as the Ca source, as the raw materials and provides a route close to that of the anticipated production line facilities. The  $\text{PuO}_2$ ,  $\text{UO}_2$  and  $\text{ThO}_2$  used in these oxide-route batches were prepared by firing nitrates of the cations at  $1050^\circ\text{C}$  in air. Based on previous experience<sup>1</sup>, wet-milled oxide-route materials will be more homogeneous than those prepared by the dry-milled oxide-route.

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<sup>1</sup> E.R. Vance, M.W.A. Stewart, R.A. Day, K.P. Hart, M.J. Hambley and A. Brownscombe, Pyrochlore-rich Titanate Ceramics for Incorporation of Plutonium, Uranium and Process Chemicals, ANSTO Report, Materials Division, R97m030, 18 November 1997

Several Pu/U-doped batches were prepared by the above methods. Some batches were prepared by an alternative route used for small batches, which employs a mixer mill (see below).

Sintering temperatures varied from 1300 to 1400°C. Sintering times of 4 hours were the process standard, with some samples heated for 75 hours to see if they approached equilibrium more closely. Argon was the standard atmosphere used. Selected samples were heated in air and 3.7 vol. % H<sub>2</sub> in Ar.

## 3 EXPERIMENTAL

### 3.1 Compositions

Compositions used are based on those forwarded by LLNL<sup>2</sup>. The compositions made using Th/U include:

- B1-2 – the baseline ceramic
- B1-4 – the baseline ceramic with impurities
- B1-10 – zirconolite-rich
- B1-12 – brannerite-rich
- B1-14 - nominally ~ 10 % perovskite
- B1-16 - ~ 10 % phosphate

Batches of the following Pu/U-doped compositions have been prepared:

- B1-1 – the baseline ceramic
- B1-9 – zirconolite-rich
- B1-3 – the baseline ceramic with impurities
- B1-11 – brannerite-rich
- B1-13 - nominally ~ 10 % perovskite
- B1-15 - ~ 10 % phosphate

The compositions of these batches as oxides are given in Tables 1 and 2. The raw materials used to make these batches are given in Tables 3 and 4.

### 3.2 Fabrication Methods

Compositions (Tables 1 and 2) were made by alkoxide-route<sup>3</sup>, oxide-route wet-mill<sup>4</sup> and oxide-route dry-mill methods<sup>5</sup>. Some of the initial batches were milled for 4 hours; however our results (see below) indicated that the milling was incomplete, so 16 hours was chosen as the standard milling time. Copies of the Work Instructions for preparing the powders are given in Appendix A.

#### 3.2.1 Alkoxide-Route Wet-milled Powder Preparation

Batches of 20 g (oxide basis) were made for each of the Th/U-doped batches. The Pu/U-doped batches B1-1, B1-9 and B1-11 were 2 g and B1-13 and B1-15 were 10 g. Composition B1-3 was made previously<sup>1</sup>.

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<sup>2</sup> Compositions used are based on those forwarded by e-mail from B.B. Ebbinghaus, LLNL, Livermore CA, in Table B1: Near equilibrium series (file B1\_Desc.xls).

<sup>3</sup> B.B. Ebbinghaus, Procedure SMP-55-98, Revision 1, Form Development Fabrication Procedure #3: Fabrication Process using Nitrates and Alkoxides, LLNL, Livermore, CA, June 21, 1998

<sup>4</sup> B.B. Ebbinghaus, Procedure SMP-55-98, Revision 2, Form Development Procedure #1 for Fabricating Immobilized Ceramic Forms: Baseline Process using Wet Ball Milling, LLNL, Livermore, CA, June 21, 1998.

<sup>5</sup> B.B. Ebbinghaus, Procedure SMP-55-98, Revision 1, Form Development Fabrication Procedure #2: Baseline Fabrication Process using Dry-milling, LLNL, Livermore, CA, June 21, 1998.





**Table 3: Raw materials used for the alkoxide batches.**

Element	Raw Materials for Alkoxide-route Batches (raw material, source, catalogue number)
Ca	99 % Ca(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O, Aldrich Chem. Co., 23712-4
Gd	99.9 % Gd(NO <sub>3</sub> ) <sub>3</sub> .6H <sub>2</sub> O, Aldrich Chem., 21159-1
Hf	99.99 % Hafnium n-butoxide, Gelest Inc.
Pu	Pu nitrate solution, (Pu-239) made by dissolving PuO <sub>2</sub> in 8M HNO <sub>3</sub> .
Th	Th(NO <sub>3</sub> ) <sub>4</sub> .5H <sub>2</sub> O, Merck, 1.08162
U	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O, depleted (~ 0.318 % U235), BDH, Batch FF296, 10289
Ti	Titanium isopropoxide, HÜLS Troisdorf GmbH., 405514
Al	99.6 % Al <sub>2</sub> O <sub>3</sub> , Degussa AG, Aluminium Oxide C
B	H <sub>3</sub> BO <sub>3</sub> , Ajax Chem., Unilab 102
Cl	CaCl <sub>2</sub> , BDH, AR grade 27587
Cr	> 99 % Cr(NO <sub>3</sub> ) <sub>3</sub> .6H <sub>2</sub> O, Fluka, 27080
F	CaF <sub>2</sub> , BDH, AR grade 540823
Fe	+ 98 % Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O, Ajax Chem., Univar 827
Ga	99.9 % Ga(NO <sub>3</sub> ) <sub>3</sub> .6H <sub>2</sub> O, Aldrich Chem., 28989-2
K	KOH, Merck, 5033
Mg	> 99 % Mg(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O, Aldrich Chem., 23717-5
Mo	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> .4H <sub>2</sub> O, May and Baker, L804
Na	NaOH, Merck, 6498
Ni	> 99 % Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O, Fluka, 72253
P	85% H <sub>3</sub> PO <sub>4</sub> , Ajax Chem.,
Si	Ludox HS-40 colloidal silica, 40% suspension in water, Aldrich Chem., 42081-6
Ta	99.9 % Ta <sub>2</sub> O <sub>5</sub> , A.D. MacKay Ltd.
W	(NH <sub>4</sub> ) <sub>10</sub> W <sub>12</sub> O <sub>41</sub> .5H <sub>2</sub> O, BDH, 27208
Zn	> 99 % Zn(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O, Fluka, 96482

**Table 4: Raw materials used for the oxide batches.**

Element	Raw Materials for Alkoxide-route Batches (raw material, source, catalogue number)
Ca	Ca(OH) <sub>2</sub> , AR grade, BDH Ltd. 90131
Gd	99.9 % Gd <sub>2</sub> O <sub>3</sub> , Paramount Chem., B913.00.40 and 99.9 %-325 mesh Gd <sub>2</sub> O <sub>3</sub> , Cerac Speciality Inorganics, G-1015
Hf	99.95 % HfO <sub>2</sub> , -325 mesh, Cerac Speciality Inorganics, H-1011
Pu	Pu nitrate solution, (Pu-239) made by dissolving PuO <sub>2</sub> in 8M HNO <sub>3</sub> .
Th	Calcined (1050°C) Th(NO <sub>3</sub> ) <sub>4</sub> .5H <sub>2</sub> O, Merck, 1.08162
U	Calcined 1050°C, UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O, depleted (~ 0.318 % U235), BDH, Batch FF296, 10289
Ti	> 99.1 % TiO <sub>2</sub> , pigment grade anatase, Tioxide Pty. Ltd., AHR select 100375.
Al	99.6 % Al <sub>2</sub> O <sub>3</sub> , Degussa AG, Aluminium Oxide C
B	H <sub>3</sub> BO <sub>3</sub> , Ajax Chem., Unilab 102
Cl	CaCl <sub>2</sub> , BDH, AR grade 27587,
Cr	Cr <sub>2</sub> O <sub>3</sub> , BDH, AR grade 218330
F	CaF <sub>2</sub> , BDH, AR grade 540823
Fe	99 % + Fe <sub>2</sub> O <sub>3</sub> , Aldrich Chem., 31005-0
Ga	99.999 % Ga <sub>2</sub> O <sub>3</sub> , Chemat Tech., RG-304
K	KOH, Merck, 5033
Mg	MgO, Johnson Matthey, Specpure J.M. 130
Mo	99.995 % MoO <sub>3</sub> , BDH, 16669
Na	NaOH, Merck, 6498
Ni	NiO, Johnson Matthey, Specpure J.M. 895
P	85% H <sub>3</sub> PO <sub>4</sub> , Ajax Chem.,
Si	Ludox HS-40 colloidal silica, 40% suspension in water, Aldrich Chem., 42081-6
Ta	99.9 % Ta <sub>2</sub> O <sub>5</sub> , A.D. MacKay Ltd.
W	99.9 % WO <sub>3</sub> , BDH, 30543
Zn	99.9 % ZnO, Aldrich Chem., 20553-2

The alkoxide precursors were made as follows. The Ti and Hf alkoxides were mixed together and diluted to 50 % by adding anhydrous ethanol. The required (Tables 1 and 2) non-radioactive chemicals (Table 3) were mixed together in deionised water and added to the alkoxides<sup>6</sup>. The batch was then shear mixed for 10 minutes. It was then taken to the uranium laboratory where uranyl nitrate was added. If the batch was a Th-doped batch, Th nitrate was added to the batch at the same time as the uranyl nitrate. If the batch was a Pu-doped batch, it was taken to the Actinide Suite for Pu nitrate addition. After these additions, the sample was stirred and then dried.

The dried powder was placed in an alumina container and calcined in air for 1 hour at 750°C.

For the 10 and 20 g batches, the calcined powder was then treated by wet ball milling (water) for 16 hours with 10 mm diameter yttria stabilised zirconia media in a nylon (Th/U-doped) or rubber jars (Pu/U-doped). Some batches were milled for 4 hours to examine the effect of milling time on equilibrium. The milled slurry was dried at 110°C.

For the 2 g batches, the calcined powder was dry-milled for 20 minutes in a 25 ml zirconia grinding jar and two 10 mm diameter zirconia balls using a MM 2 mixer mill<sup>7</sup>.

### 3.2.2 Oxide-Route Wet-milled Powder Preparation

The oxide precursors were made as follows. The non-radioactive elements were mixed together in a plastic jar taken to the uranium laboratory where UO<sub>2</sub> was added. If the batch was a Th-doped batch, ThO<sub>2</sub> was also added to the batch at the same time as the UO<sub>2</sub>. If the batch was a Pu-doped batch, it was taken to the Actinide Suite for PuO<sub>2</sub> addition. The powders were blended by tumbling the jar.

The blended powder was placed in an alumina container calcined for 1 hour at 750°C in air.

The calcined powders were placed in rubber or nylon jars with 10 mm diameter yttria stabilised zirconia media and wet ball milled in water for 16 hours. Some batches were milled for 4 hours to examine the effect of milling time on equilibrium. The milled slurry was dried at 110°C.

### 3.2.3 Oxide-Route Dry-milled Powder Preparation

The blended oxide-route powders were made as above (section 3.2.2) and calcined in an alumina container for 1 hour at 750°C in air.

The calcined powders, jars<sup>8</sup> and media were dried ~ 120°C prior to dry ball milling. Dry-milling was carried out in rubber (Pu/U-doped) or nylon jars (Th/U-doped) with 10 mm diameter yttria stabilised zirconia media for 16 hours. Some batches were milled for 4 hours to examine the effect of milling time on equilibrium. The milled slurry was dried at 110°C.

### 3.2.4 Cold-pressing and Sintering

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<sup>6</sup> Amount of water is 4 times the weight of alkoxide.

<sup>7</sup> Model MM 2 Mixer mill, Retsch GmbH, Rheinische Strasse 36, Haan, Germany. Grinding jar used was a 25 ml zirconia jar with cover – Retsch code 01.462.0047. Two 12 mm dia. zirconia balls were used to grind the powder – Retsch code 05.369.0023.

<sup>8</sup> Rubber milling jars were not dried at 110°C.

Pellets were prepared by cold pressing ~ 0.5 g of powder in a 10mm diameter steel die at ~ 60 MPa. Dies were lubricated with oleic acid.

Batches B1-14 and B-16, made by the oxide-route laminated during the initial pressing runs. Therefore, PEG 400 was added to these batches as a binder/lubricant, to eliminate laminations. This PEG was added to the powder just prior to pressing using a mortar and pestle for mixing.

The green pellets were sintered in an alumina tube furnace. Sintering atmospheres used were 0.25 l/min. of: Ar, air or 3.7 % H<sub>2</sub> in Ar. Argon was the standard atmosphere. The standard sintering time was 4 hours, though some samples were sintered for 75 hours. The standard sintering temperature was 1350°C with selected samples being fired at 1300 and 1400°C. The heating and cooling rates were 5°C/min.

### **3.3 Analysis**

After sintering, the densities of the samples were measured using Archimedes' method, in water for the Th/U-doped samples and octanol for the Pu/U-doped samples, via the evacuation method.

The samples were then mounted in resin and polished to a 0.25-1.0 μm diamond finish. The polished surface was examined by X-ray diffraction (XRD), using either a Siemens D500 diffractometer employing Co K-alpha radiation, or a Scintag X1 Advanced Diffractometer System, with Cu K-alpha radiation. The samples were examined by scanning electron microscopy (SEM) using either a JEOL JSM6400 or JEOL JSM6300 machines, both of which are fitted with energy dispersive x-ray spectrometry (EDS) instruments for quantitative analysis.

## 4 RESULTS AND DISCUSSION

Summary X-ray diffraction (XRD) results and the raw XRD data file names for Task 1.2 are given in Appendix B.

### 4.1 Densities

The green densities of the oxide-route batches were typically  $3.0 \pm 0.2 \text{ g/cm}^3$  (Table 5). The 4 hour mill batches had a lower green density than the 16 hour milled batches. The green densities of the alkoxide-route batches were lower than the oxide-route batches.

The alkoxide-route batches pressed easily to make good pellets. The oxide-route pellets were harder to press and often laminated. This could be overcome by moistening the powder with water. For the oxide-route powders from compositions B1-14 and B1-16 some pellets were made with PEG 400 addition (added using a mortar and pestle). This was successful in reducing lamination.

Fired density data are given in Tables 5 and 6. The following trends were observed:

- The dry-milled pellets were generally less dense and had higher porosities.
- The alkoxide batches, except the batch with composition B1-3 or B1-4, had more porosity than the wet-milled oxide-route samples.
- All the pellets made from batches with process impurities sintered to a high density with low porosity.
- Pellets made from 4 hour milled batches had lower densities than the equivalent pellets made from the 16 hour milled batches.
- The Pu/U-doped samples are denser than the Th/U-doped samples. This could be due to the relative reactivity of the  $\text{ThO}_2$  and  $\text{PuO}_2$ ;  $\text{ThO}_2$  is more refractory than  $\text{PuO}_2$ .
- The oxide-route wet-milled batches are sinterable to closed porosity (typically  $< \sim 5\%$  open porosity).

Density comparisons between the Th/U-doped batches are more difficult due to variations in phase composition and hence theoretical density.

**Table 5: Densities of the Th/U-doped samples**

Pellet No.	Composition	Route	Wet or Dry	Milling Time (h.)	Sint. Temp. (°C)	Time (h.)	Atm.	Green Density (g/cm <sup>3</sup> )	Sint. Density (g/cm <sup>3</sup> )	Apparent Porosity (%)
mws980106	B1-2	Alkoxide	Wet	4	1350	4	Ar		4.90	8.4
mws980107	B1-2	Alkoxide	Wet	4	1350	4	Ar		4.96	6.2
mws980172	B1-2	Alkoxide	Wet	16	1350	4	Ar	2.5	5.29	0.3
mws980173	B1-2	Alkoxide	Wet	16	1350	4	Ar	2.5	5.25	0.2
mws980348	B1-2	Alkoxide	Wet	16	1350	75	Ar		5.15	0.2
mws980296	B1-2	Alkoxide	Wet	16	1350	4	3.7%H <sub>2</sub> /Ar	2.4	5.47	1.5
mws980297	B1-2	Alkoxide	Wet	16	1350	4	3.7%H <sub>2</sub> /Ar	2.5	5.53	1.5
mws980308	B1-2	Alkoxide	Wet	16	1300	4	Ar	2.4	5.31	2.0
mws980309	B1-2	Alkoxide	Wet	16	1300	4	Ar	2.4	5.32	5.1
mws980322	B1-2	Alkoxide	Wet	16	1400	4	Ar	2.4	5.00	1.8
mws980323	B1-2	Alkoxide	Wet	16	1400	4	Ar	2.5	4.79	3.8
mws980134	B1-2	Oxide	Dry	4	1350	4	Ar	2.9	4.70	17.9
mws980139	B1-2	Oxide	Dry	16	1350	4	Ar	3.1	4.91	13.7
mws980140	B1-2	Oxide	Dry	16	1350	4	Ar	3.1	4.92	13.8
mws980133	B1-2	Oxide	Wet	4	1350	4	Ar	2.8	5.04	11.4
mws980137	B1-2	Oxide	Wet	16	1350	4	Ar	2.9	5.62	0.5
mws980138	B1-2	Oxide	Wet	16	1350	4	Ar	3.0	5.57	0.2
mws980391	B1-2	Oxide	Wet	16	1350	75	Ar	2.7	5.41	5.6
mws980407	B1-2	Oxide	Wet	16	1400	4	Ar	2.1	5.44	1.6
mws980112	B1-4	Alkoxide	Wet	4	1350	4	Ar		5.42	0.3
mws980113	B1-4	Alkoxide	Wet	4	1350	4	Ar		5.46	0.0
mws980176	B1-4	Alkoxide	Wet	16	1350	4	Ar	2.3	5.34	1.3
mws980177	B1-4	Alkoxide	Wet	16	1350	4	Ar	2.4	5.32	1.4
mws980350	B1-4	Alkoxide	Wet	16	1350	75	Ar		5.15	3.0
mws980316	B1-4	Alkoxide	Wet	16	1300	4	Ar	2.4	5.30	5.1
mws980317	B1-4	Alkoxide	Wet	16	1300	4	Ar	2.3	5.08	7.4
mws980302	B1-4	Alkoxide	Wet	16	1400	4	Ar	2.3	5.21	1.9
mws980303	B1-4	Alkoxide	Wet	16	1400	4	Ar	2.3	5.08	3.6
mws980151	B1-4	Oxide	Dry	16	1350	4	Ar	3.1	4.97	10.5
mws980152	B1-4	Oxide	Dry	16	1350	4	Ar	3.1	5.19	8.0
mws980149	B1-4	Oxide	Wet	16	1350	4	Ar	3.0	5.23	0.6
mws980150	B1-4	Oxide	Wet	16	1350	4	Ar	3.0	5.28	0.4
mws980394	B1-4	Oxide	Wet	16	1350	75	Ar	2.8	4.99	3.7
mws980408	B1-4	Oxide	Wet	16	1400	4	Ar	2.5	5.11	1.7

Pellet No.	Composition	Route	Wet or Dry	Milling Time (h.)	Sint. Temp. (°C)	Time (h.)	Atm.	Green Density (g/cm <sup>3</sup> )	Sint. Density (g/cm <sup>3</sup> )	Apparent Porosity (%)
mws980108	B1-10	Alkoxide	Wet	4	1350	4	Ar		4.87	11.8
mws980109	B1-10	Alkoxide	Wet	4	1350	4	Ar		4.80	13.2
mws980174	B1-10	Alkoxide	Wet	16	1350	4	Ar	2.1	5.13	5.1
mws980175	B1-10	Alkoxide	Wet	16	1350	4	Ar	2.3	5.21	3.1
mws980298	B1-10	Alkoxide	Wet	16	1350	4	3.7%H <sub>2</sub> /Ar	2.3	5.18	5.5
mws980299	B1-10	Alkoxide	Wet	16	1350	4	3.7%H <sub>2</sub> /Ar	2.2	5.26	3.9
mws980349	B1-10	Alkoxide	Wet	16	1350	75	Ar		5.29	1.4
mws980310	B1-10	Alkoxide	Wet	16	1300	4	Ar	2.3	4.85	13.5
mws980311	B1-10	Alkoxide	Wet	16	1300	4	Ar	2.3	4.68	16.9
mws980324	B1-10	Alkoxide	Wet	16	1400	4	Ar	2.3	4.98	5.1
mws980325	B1-10	Alkoxide	Wet	16	1400	4	Ar	2.3	5.11	2.3
mws980147	B1-10	Oxide	Dry	16	1350	4	Ar	3.3	4.14	28.8
mws980148	B1-10	Oxide	Dry	16	1350	4	Ar	3.3	4.10	29.3
mws980145	B1-10	Oxide	Wet	16	1350	4	Ar	3.0	4.74	18.1
mws980146	B1-10	Oxide	Wet	16	1350	4	Ar	2.8	4.56	22.0
mws980395	B1-10	Oxide	Wet	16	1350	75	Ar	3.1	5.02	8.0
mws980409	B1-10	Oxide	Wet	16	1400	4	Ar	2.0	5.94	2.8
mws980110	B1-12	Alkoxide	Wet	4	1350	4	Ar		4.78	0.5
mws980111	B1-12	Alkoxide	Wet	4	1350	4	Ar		4.72	0.8
mws980178	B1-12	Alkoxide	Wet	16	1350	4	Ar	2.4	4.62	2.9
mws980179	B1-12	Alkoxide	Wet	16	1350	4	Ar	2.4	4.64	2.4
mws980351	B1-12	Alkoxide	Wet	16	1350	75	Ar		4.11	20.8
mws980300	B1-12	Alkoxide	Wet	16	1350	4	3.7%H <sub>2</sub> /Ar	2.3	5.28	2.7
mws980301	B1-12	Alkoxide	Wet	16	1350	4	3.7%H <sub>2</sub> /Ar	2.0	5.44	0.9
mws980312	B1-12	Alkoxide	Wet	16	1300	4	Ar	2.4	5.15	1.4
mws980313	B1-12	Alkoxide	Wet	16	1300	4	Ar	2.4	5.23	1.9
mws980326	B1-12	Alkoxide	Wet	16	1400	4	Ar	2.4	4.31	2.0
mws980327	B1-12	Alkoxide	Wet	16	1400	4	Ar	2.4	4.31	2.1
mws980143	B1-12	Oxide	Dry	16	1350	4	Ar	3.1	4.61	17.7
mws980144	B1-12	Oxide	Dry	16	1350	4	Ar	3.1	4.61	17.0
mws980141	B1-12	Oxide	Wet	16	1350	4	Ar	3.1	5.65	1.6
mws980142	B1-12	Oxide	Wet	16	1350	4	Ar	3.0	5.64	0.9
mws980396	B1-12	Oxide	Wet	16	1350	75	Ar	2.6	5.55	5.8
mws980410	B1-12	Oxide	Wet	16	1400	4	Ar		5.53	3.2

Pellet No.	Composition	Route	Wet or Dry	Milling Time (h.)	Sint. Temp. (°C)	Time (h.)	Atm.	Green Density (g/cm <sup>3</sup> )	Sint. Density (g/cm <sup>3</sup> )	Apparent Porosity (%)
mws980261	B1-14	Alkoxide	Wet	16	1350	4	Ar	2.3	5.00	3.5
mws980262	B1-14	Alkoxide	Wet	16	1350	4	Ar	2.4	4.83	1.7
mws980267	B1-14	Alkoxide	Wet	16	1350	4	air	2.4	4.72	2.3
mws980268	B1-14	Alkoxide	Wet	16	1350	4	air	2.4	4.59	5.0
mws980392	B1-14	Alkoxide	Wet	16	1350	75	Ar	2.5	4.38	8.8
mws980318	B1-14	Alkoxide	Wet	16	1300	4	Ar	2.3	4.51	16.8
mws980319	B1-14	Alkoxide	Wet	16	1300	4	Ar	2.4	4.65	14.9
mws980304	B1-14	Alkoxide	Wet	16	1400	4	Ar	2.4	4.56	2.3
mws980305	B1-14	Alkoxide	Wet	16	1400	4	Ar	2.4	4.58	1.6
mws980259	B1-14	Oxide	Dry	16	1350	4	Ar	3.1	4.50	23.4
mws980260	B1-14	Oxide	Dry	16	1350	4	Ar	2.9	4.58	19.9
mws980283 <sup>s</sup>	B1-14	Oxide	Dry	16	1350	4	Ar	2.9	4.18	27.3
mws980284 <sup>s</sup>	B1-14	Oxide	Dry	16	1350	4	Ar	2.9	4.00	31.3
mws980265	B1-14	Oxide	Dry	16	1350	4	air	3.0	3.76	32.9
mws980266	B1-14	Oxide	Dry	16	1350	4	air	3.0	3.83	31.9
mws980287 <sup>s</sup>	B1-14	Oxide	Dry	16	1350	4	air	2.8	4.06	25.4
mws980288 <sup>s</sup>	B1-14	Oxide	Dry	16	1350	4	air	2.7	4.22	24.2
mws980257	B1-14	Oxide	Wet	16	1350	4	Ar	2.7	5.10	3.1
mws980258	B1-14	Oxide	Wet	16	1350	4	Ar	2.8	5.18	1.5
mws980281 <sup>s</sup>	B1-14	Oxide	Wet	16	1350	4	Ar	3.0	4.85	6.4
mws980282 <sup>s</sup>	B1-14	Oxide	Wet	16	1350	4	Ar	3.1	4.88	4.9
mws980263	B1-14	Oxide	Wet	16	1350	4	air	2.5	4.78	6.4
mws980264	B1-14	Oxide	Wet	16	1350	4	air	2.6	4.88	5.2
mws980285 <sup>s</sup>	B1-14	Oxide	Wet	16	1350	4	air	3.1	5.13	0.8
mws980286 <sup>s</sup>	B1-14	Oxide	Wet	16	1350	4	air	3.2	5.12	2.0
mws980397 <sup>s</sup>	B1-14	Oxide	Wet	16	1350	75	Ar	2.8	5.32	1.0
mws980411 <sup>s</sup>	B1-14	Oxide	Wet	16	1400	4	Ar		5.28	2.3
mws980273	B1-16	Alkoxide	Wet	16	1350	4	Ar	2.4	3.62	29.3
mws980274	B1-16	Alkoxide	Wet	16	1350	4	Ar	2.3	3.62	29.3
mws980279	B1-16	Alkoxide	Wet	16	1350	4	air	2.2	4.78	2.2
mws980280	B1-16	Alkoxide	Wet	16	1350	4	air	2.2	4.69	2.3
mws980393	B1-16	Alkoxide	Wet	16	1350	75	Ar	2.3	3.70	28.3
mws980320	B1-16	Alkoxide	Wet	16	1300	4	Ar	2.3	4.75	2.6
mws980321	B1-16	Alkoxide	Wet	16	1300	4	Ar	2.3	4.85	1.1
mws980306	B1-16	Alkoxide	Wet	16	1400	4	Ar	2.3	4.73	7.3
mws980307	B1-16	Alkoxide	Wet	16	1400	4	Ar	2.3	4.91	1.2
mws980271 <sup>s</sup>	B1-16	Oxide	Dry	16	1350	4	Ar	2.9	3.98	26.4
mws980272 <sup>s</sup>	B1-16	Oxide	Dry	16	1350	4	Ar	2.9	3.89	27.0
mws980277 <sup>s</sup>	B1-16	Oxide	Dry	16	1350	4	air	2.9	friable	
mws980278 <sup>s</sup>	B1-16	Oxide	Dry	16	1350	4	air	3.0	2.92 friable	52.2
mws980269 <sup>s</sup>	B1-16	Oxide	Wet	16	1350	4	Ar	2.8	4.66	17.0
mws980270 <sup>s</sup>	B1-16	Oxide	Wet	16	1350	4	Ar	2.9	4.82	14.0
mws980275 <sup>s</sup>	B1-16	Oxide	Wet	16	1350	4	air	2.8	5.26	2.1
mws980276 <sup>s</sup>	B1-16	Oxide	Wet	16	1350	4	air	2.8	5.10	3.8
mws980398 <sup>s</sup>	B1-16	Oxide	Wet	16	1350	75	Ar	2.8	5.23	4.5
mws980412 <sup>s</sup>	B1-16	Oxide	Wet	16	1400	4	Ar		5.37	2.4

§ PEG 400 binder-lubricant added to these powders prior to cold-pressing

**Table 6: Densities of the Pu/U-doped samples fired at for 4 h in Ar. All samples milled for 16 hours.**

Batch No.	Composition	Route	Wet or Dry Mill	Sint. Temp (°C)	Sint. Density (g/cm <sup>3</sup> )	Apparent Porosity (%)
Pu92	B1-1	Alkoxide	MM2 mill	1350	+	
Pu67 #	B1-1	Oxide	Dry	1300	5.37	0.06
Pu67 #	B1-1	Oxide	Dry	1325	5.34	0.22
Pu67 #	B1-1	Oxide	Dry	1350	5.57	0.02
Pu67 #	B1-1	Oxide	Dry	1375	5.45	0.27
Pu67 #	B1-1	Oxide	Dry	1400	5.41	0.21
Pu68 #	B1-1	Oxide	Wet	1300	5.61	0.00
Pu68 #	B1-1	Oxide	Wet	1325	5.60	0.11
Pu68 #	B1-1	Oxide	Wet	1350	5.40	0.19
Pu68 #	B1-1	Oxide	Wet	1375	5.55	0.12
Pu68 #	B1-1	Oxide	Wet	1400	5.40	0.15
Pu73 #	B1-3 (A-9)	Alkoxide	Wet	1300	5.61	0.09
Pu71 #	A-7	Alkoxide	MM2 mill	1300	4.96	0.02
Pu75 #	A-7	Oxide	Wet	1325	5.54	0.00
Pu93	B1-9	Alkoxide	MM2 mill	1350	+	
Pu98	B1-9	Oxide	Dry	1350	5.70	0.08
Pu97	B1-9	Oxide	Wet	1350	5.71	0.00
Pu94	B1-11	Alkoxide	MM2 mill	1350	+	
Pu100	B1-11	Oxide	Dry	1350	5.70	0.17
Pu99	B1-11	Oxide	Wet	1350	5.60	0.10
Pu105	B1-13	Alkoxide	Wet	1350	4.98	0.06
Pu102	B1-13	Oxide	Dry	1350	5.48	0.00
Pu101	B1-13	Oxide	Wet	1350	5.29	0.12
Pu106	B1-15	Alkoxide	Wet	1350	3.75	0.21
Pu104	B1-15	Oxide	Dry	1350	5.21	0.32
Pu103	B1-15	Oxide	Wet	1350	5.35	0.03

# Done as part of Reference in footnote 1

+ Still to be Measured

## 4.2 Th/U-doped Samples

As can be seen in the EDS results, given in Appendices C-H, the Th/U-brannerite is enriched<sup>9</sup> in Th relative to the bulk composition. The Pu/U-doped samples made for this project (section 4.3) or those made in 1997<sup>1</sup> were not enriched in Pu relative to the matrix. The result is that minor variations in phase makeup between the Th-doped and Pu-doped batches exist.

### 4.2.1 Composition B1-2 - Baseline

The XRD results on samples made from composition B1-2 are given in Appendix B and SEM micrographs and EDS results are given in Appendix C.

#### 4.2.1.1 Composition B1-2 sintered at 1350°C in Ar for 4 hours

##### 4.2.1.1.1 B1-2 Alkoxide wet-mill 4 hours

*Sample mws980106* (Appendix C, Table C-1 and Figure C-1) - The pellet was heterogeneous (fig. C-1a), consisting of regions of high density that are deficient in rutile, and porous regions. Phases detected were:

- pyrochlore
- ~ 10 – 20 vol. % Th/U-brannerite
- ~ 5 vol. % Hf-doped rutile

The Th/U- brannerite was variable in composition across the sample.

##### 4.2.1.1.2 B1-2 Alkoxide wet-mill 16 hours

*Sample mws980173* (Appendix C, Table C-1 and Figure C-2) – The sample consists of:

- pyrochlore
- ~ 10 - 15 vol. % Th/U-brannerite
- ~ 5 vol. % Hf-doped rutile

Porosity, ~ 1 to 5 μm in diameter, was also present. The sample is much more homogeneous than the 4 hour mill sample (Fig. C-1).

Pellets made from the 16 hour milled batch consisted of the same phases as the 4 hour mill batch section and did not have the heterogeneous (porous/dense regions). The porosity was more evenly dispersed. The rutile contained some Hf and small amounts of Ca, Th and U (Table C-2). The pyrochlore has a composition close to the target composition, but is slightly deficient in Th. Apart from this, the pyrochlore is very similar in composition to the baseline Pu-doped pyrochlore made in 1997<sup>1</sup> (see also section 4.3.1).

##### 4.2.1.1.3 B1-2 Oxide dry-mill 4 hours

*Sample mws980134* (Appendix C, Table C-2 and Figure C-3) - The pellet was heterogeneous on a mm scale. It contained large lumps (up to ~ 20 μm across) of ThO<sub>2</sub> surrounded by Th/U-brannerite. Phases detected were:

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<sup>9</sup> The U to Th and the U to Pu ratios in these batches should be 2:1.

- pyrochlore
- ~ 20 – 25 vol. % Th/U-brannerite. The Th/U- brannerite was variable in composition and contained some Hf and Gd.
- ~ 10 – 20 vol. % 2M zirconolite
- ~ 5 vol. % ThO<sub>2</sub>
- ~ 5 vol. % Hf-doped rutile
- << 1 vol. % whitlockite<sup>10</sup>

Pellets made from the 4 hour dry-milled batch were very porous and consisted mainly of pyrochlore, with some 2M zirconolite and regions of Th/U-brannerite 10-40 μm across, the larger of which have a core of thoria (fig. C-3). Hf-doped rutile and traces of 4M zirconolite were also present. Traces of a phosphate phase (whitlockite) were detected. The deficiency in Th, due to significant amounts of the Th remaining as ThO<sub>2</sub>, has resulted in zirconolite formation

#### **4.2.1.1.4 B1-2 Oxide dry-mill 16 hours**

*Sample mws980139* (Appendix C, Table C-2 and Figure C-4) - Phases detected were:

- pyrochlore
- ~ 20 – 25 vol. % Th/U-brannerite, the Th/U- brannerite was variable in composition and contained some Hf and Gd.
- ~ 5 - 10 vol. % of what is believed to be 4M zirconolite
- ~ 5 vol. % Hf-doped rutile
- ~ 5 vol. % ThO<sub>2</sub>
- << 1 vol. % whitlockite<sup>10</sup>

Additional milling, to give a total of 16 hours milling, did not appear to make a significant difference to the microstructure. The formation of zirconolite is probably due to the low reactivity of the high-fired ThO<sub>2</sub>. This enriches the matrix in Hf (relative to Σ U+Gd+Th) resulting in the formation of zirconolite and a pyrochlore, which is slightly enriched in Hf. The compositions of the phases vary across the microstructure.

#### **4.2.1.1.5 B1-2 Oxide wet-mill 4 hours**

*Sample mws980133* (Appendix C, Table C-3 and Figure C-5) - Phases detected were:

- pyrochlore
- ~ 25 – 30 vol. % Th/U-brannerite of variable composition
- ~ 5 - 10 vol. % of what is believed to be 4M zirconolite
- ~ 5 vol. % Hf-doped rutile
- ~ 2 vol. % ThO<sub>2</sub>
- << 1 vol. % whitlockite<sup>10</sup>

The pellets were variable in composition on a mm scale – due to incomplete milling.

#### **4.2.1.1.6 B1-2 Oxide wet-mill 16 hours**

*Sample mws980137* (Appendix C, Table C-3 and Figure C-6) - Phases detected were:

- pyrochlore
- ~ 20 - 25 vol. % Th/U-brannerite
- ~ 5 vol. % of what is believed to be 4M zirconolite

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<sup>10</sup> The phosphorus comes from the anatase powder used as the TiO<sub>2</sub> source.

- ~ 3 vol. % Hf-doped rutile
- ~ 1 vol. % ThO<sub>2</sub>
- << 1 vol. % whitlockite<sup>10</sup>

Milling for 16 hours, instead of 4 hours, substantially improved the homogeneity. The amount of Th/U-brannerite in the pellets was reduced. Submicron ThO<sub>2</sub> (< 1 vol. %) was present in some of the larger Th/U-brannerite regions.

#### **4.2.1.2 Composition B1-2 alkoxide-route sintered at 1300°C in Ar for 4 hours**

*Sample mws980309* (Appendix C, Table C-4 and Figure C-7) - The microstructure is similar but finer than that of the pellets sintered at 1350°C in Ar (section 4.2.1.1.2). The 1300°C sinter has a microstructure consisting of:

- pyrochlore, which is similar in composition to that in the 1350°C pellet
- ~ 15 - 20 vol % Th/U-brannerite
- ~ 5 vol. % Hf-doped rutile.
- ~ 2 - 5 vol. % of what is believed to be 4M zirconolite

The Th/U-brannerite composition is slightly variable from grain to grain. Like the 1350°C sinter, the Th is enriched in the Th/U-brannerite, relative to the matrix. Some 4M zirconolite (~ 5 vol. %), this was present, which was not detected in the 1350°C pellet. This indicates that the reaction at 1300°C is incomplete after 4 hours.

#### **4.2.1.3 Composition B1-2 alkoxide-route sintered at 1400°C in Ar for 4 hours**

*Sample mws980323* (Appendix C, Table C-4 and Figure C-8) - The microstructure consists of:

- pyrochlore
- ~ 10 - 15 vol % Th/U-brannerite
- ~ 2 vol. % Hf-doped rutile

The microstructure is similar but coarser than that of the samples sintered at 1300 or 1350°C in Ar (sections 4.2.1.2 and 4.2.1.1.2).

#### **4.2.1.4 Composition B1-2 oxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours**

*Sample mws980407* (Appendix C, Table C-5 and Figure C-9) - The microstructure consists of:

- pyrochlore
- ~ 15 - 20 vol % Th/U-brannerite
- < 1 vol. % (Th,U)O<sub>2</sub>, located inside brannerite grains

The sample did not contain rutile, which is similar to the result when this powder was sintered for 75 hours at 1350°C (section 4.2.1.6).

#### **4.2.1.5 Composition B1-2 alkoxide-route sintered at 1350°C for 75 hours in Ar**

*Sample mws980348* (Appendix C, Table C-4 and Figure C-10) - The microstructure consists of:

- pyrochlore, having a composition of similar to the that in 1350°C pellet
- ~ 10 - 15 vol % Th/U-brannerite
- ~ 3 vol. % Hf-doped rutile

The microstructure is similar but coarser than that of the samples sintered at 1350°C in Ar for 4 hours (section 4.2.1.1.2).

#### **4.2.1.6 Composition B1-2 oxide-route, wet-milled 16 hours, sintered at 1350°C for 75 hours in Ar**

*Sample mws980391* (Appendix C, Table C-5 and Figure C-11) - The microstructure consists of:

- pyrochlore, having a composition of similar to that in the 1350°C pellet
- ~ 15 vol % Th/U-brannerite
- << 1 vol. % whitlockite<sup>10</sup>

Rutile was not detected in the sample, which is similar to the oxide-route sample sintered at 1400°C (section 4.2.1.4). The alkoxide route samples sintered at 1350°C for 75 hours and 1400°C (sections 4.2.1.3 and 4.2.1.5) also had less rutile. The microstructure is coarser than that of the sample sintered at 1350°C in Ar for 4 hours (section 4.2.1.1.6).

### **4.2.2 Composition B1-4 – Baseline + Impurities**

The XRD results on samples made from composition B1-4 are given in Appendix B and SEM micrographs and EDS results are given in Appendix D. There were two major compositional differences between this composition and the baseline. Firstly, zirconolite (2M) has formed due to the impurity addition, e.g., Fe, Al and Ga, all of which promote zirconolite formation at the expense of pyrochlore. Secondly, a silicate phase, probably a glassy phase, has formed at the triple points and grain boundaries. The latter has the effect of improving the sinterability and homogeneity of the samples, but it also caused some warping of the fired pellets at 1350°C and above.

#### **4.2.2.1 Composition B1-4 sintered at 1350°C in Ar for 4 hours**

##### **4.2.2.1.1 B1-4 Alkoxide wet-mill 4 hours**

*Sample mws980112* (Appendix D, Table D-1 and Figure D-1) – The sample consisted of:

- pyrochlore
- ~ 15-20 vol. % Th/U-brannerite
- ~ 7 - 10 vol. % 2M zirconolite
- ~ 1 - 2 vol. % of a silicate phase (Si-Ca-Mg-Na-K-Ti-Al-Ga-O), probably a glass

There may be some 4M zirconolite present (associated with the pyrochlore) however the crystallite size was too small to analyse. The grain size is larger than that in the baseline ceramic and the rounding of the grains suggests the presence of a liquid phase during sintering. The impurities appear to have aided sintering and the heterogeneity seen in the baseline ceramic (section 4.2.1.1.1, above) is absent.

##### **4.2.2.1.2 B1-4 Alkoxide wet-mill 16 hours**

*Sample mws980177* (Appendix D, Table D-1 and Figure D-2) – The sample consisted of:

- pyrochlore
- ~ 7 - 10 vol. % 2M zirconolite
- ~ 7 - 10 vol. % Th/U-brannerite
- ~ 1 vol. % of a silicate phase (Si-Ca-Mg-Na-K-Ti-Al-Ga-O), probably a glass

The sample made from the 16 hour milled batch is similar to that of the 4 hour mill sample (section 4.2.2.1.1). The grain size, however, appears to be more uniform and slightly smaller in the 16 hour milled sample. 4M zirconolite was not detected in this sample. There is less Th/U-brannerite present (~ 10 vol. % compared to ~ 15-20 vol. % in the 4 hour mill). The microstructure is similar to that of the Pu-doped sample made by a similar method in 1997<sup>1</sup>.

#### **4.2.2.1.3 B1-4 Oxide dry-mill 16 hours**

*Sample mws980151* (Appendix D, Table D-2 and Figure D-3) – The sample consisted of:

- pyrochlore
- ~ 10 vol. % Th/U-brannerite
- ~ 10 vol. % 2M zirconolite
- ~ 1 - 2 vol. % of a silicate phase (Si-Ca-Mg-Na-K-Ti-Al-Ga-O), probably a glass

The sample has some large pores, ~ 5 – 15  $\mu\text{m}$  in diameter, but is more homogeneous than the dry-milled baseline ceramic without additives (section 4.2.1.1.4). The grain size is larger, than that in the equivalent baseline ceramic and their shape suggests liquid phase sintering was acting during firing. No  $\text{ThO}_2$  was detected.

The microstructure is similar to the alkoxide-route pellet (section 4.2.2.1.2), except that the brannerite regions are larger, about 40  $\mu\text{m}$  across compared to ~ 5  $\mu\text{m}$  for the alkoxide-route pellets.

#### **4.2.2.1.4 B1-4 Oxide wet-mill 16 hours**

*Sample mws980149* (Appendix D, Table D-2 and Figure D-4 – The sample consisted of:

- pyrochlore
- ~ 10 vol. % Th/U-brannerite
- ~ 10 vol. % 2M zirconolite
- ~ 1 - 2 vol. % of a silicate phase (Si-Ca-Mg-Na-K-Ti-Al-Ga-O), probably a glass

Oxide-route wet-mill pellets are similar to the alkoxide-route pellets (section 4.2.2.1.2), except that there is slightly more Th/U-brannerite present in the oxide-route batch (fig. 8).

#### **4.2.2.2 Composition B1-4 alkoxide-route sintered at 1300°C in Ar for 4 hours**

*Sample mws980317* (Appendix D, Table D-3 and Figure D-5) – The sample consisted of:

- pyrochlore
- ~ 10 - 15 vol. % 2M zirconolite
- ~ 15 vol. % Th/U-brannerite
- ~ 1 - 2 vol. % of a silicate phase
- << 1 vol. %  $\text{ThO}_2$

The sample fired at 1300°C is similar to the 1350 and 1400°C samples, but has a finer grain size (sections 4.2.2.1.2 and 4.2.2.3). There may be slightly more Th/U-brannerite.

Like the 1350°C sinter the Th is enriched in the Th/U-brannerite, relative to the matrix. The 2M zirconolite contains some of the impurity elements, namely, Mg, Fe, Cr, Ga, Al. Al, Mg, Ta and W were detected in the pyrochlore. Some (<< 1 vol. %) “unreacted”  $\text{ThO}_2$  < 0.5  $\mu\text{m}$  across is present in some of the Th/U-brannerite grains.

#### 4.2.2.3 Composition B1-4 alkoxide-route sintered at 1400°C in Ar for 4 hours

*Sample mws980303* (Appendix D, Table D-3 and Figure D-6 – The sample consisted of:

- pyrochlore
- ~ 10 - 15 vol. % 2M zirconolite
- ~ 10 vol. % Th/U-brannerite
- ~ 1 - 2 vol. % of a silicate phase

The pellet sintered at 1400°C is similar to the pellet sintered at 1350°C (section 4.2.2.1.2), but has coarser grains than the 1350°C sintered pellet.

#### 4.2.2.4 Composition B1-4 oxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours

*Sample mws980408* (Appendix D, Table D-4 and Figure D-7 – The sample consisted of:

- pyrochlore
- ~ 10 - 15 vol. % 2M zirconolite
- ~ 10 vol. % Th/U-brannerite
- ~ 1 - 2 vol. % of a silicate phase
- < 1 vol. % (Th,U)O<sub>2</sub>, located inside brannerite grains.

The pellet sintered at 1400°C is similar to the pellet sintered at 1350°C (section 4.2.2.1.4), but has coarser grains than the 1350°C sintered pellet.

#### 4.2.2.5 Composition B1-4 alkoxide-route sintered at 1350°C in Ar for 75 hours

*Sample mws980351* (Appendix D, Table D-3 and Figure D-8) – The sample consisted of:

- pyrochlore
- ~ 10 - 15 vol. % 2M zirconolite
- ~ 10 vol. % Th/U-brannerite
- ~ 1 - 2 vol. % of a silicate phase

The pellet is similar to the alkoxide-route pellet sintered at 1350°C for 4 hours in Ar (section 4.2.2.1.2), but has coarser grains.

#### 4.2.2.6 Composition B1-4 oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours

*Sample mws980394* (Appendix D, Table D-4 and Figure D-8) – The sample consisted of:

- pyrochlore
- ~ 10 - 15 vol. % 2M zirconolite
- ~ 10 vol. % Th/U-brannerite
- ~ 1 - 2 vol. % of a silicate phase
- < 1 vol. % ThO<sub>2</sub>, located within some of the brannerite grains

The pellet is similar to the oxide-route pellet sintered at 1350°C for 4 hours in Ar (section 4.2.2.1.2), but has coarser grains.

### 4.2.3 Composition B1-10 – Zirconolite-rich

The XRD results on samples made from composition B1-10 are given in Appendix B and SEM micrographs and EDS results are given in Appendix E.

As expected from the formulation these samples contain large amounts, ~ 40 - 50 vol. %, of zirconolite. The samples essentially consist of a pyrochlore-zirconolite matrix with secondary phases such as brannerite, dispersed through the matrix.

#### 4.2.3.1 Composition B1-10 sintered at 1350°C in Ar for 4 hours

##### 4.2.3.1.1 B1-10 Alkoxide wet-mill 4 hours

*Sample mws980108* (Appendix E, Table E-1 and Figure E-1) – This sample consisted of:

- pyrochlore
- ~ 30 - 40 vol. % 2M zirconolite
- ~ 20 vol. % Th/U-brannerite

The composition of the phases was variable across the pellet indicating incomplete milling.

##### 4.2.3.1.2 B1-10 Alkoxide wet-mill 16 hours

*Sample mws980175* (Appendix E, Table E-1 and Figure E-2) – This sample consisted of:

- pyrochlore
- ~ 35 - 40 vol. % 2M zirconolite
- ~ 15 vol. % Th/U-brannerite

The microstructure of pellets made from the 16 hour mill batch (section 4.2.3.1.1) is more uniform than the 4 hour mill batch, with the same phases being present. There is slightly less brannerite in this sample than in the 4 hour mill sample.

##### 4.2.3.1.3 B1-10 Oxide dry-mill 16 hours

*Sample mws980147* (Appendix E, Table E-2 and Figure E-3) – This sample was inhomogeneous. It consisted of:

- pyrochlore
- ~ 30 vol. % 2M zirconolite
- ~ 20 vol. % Th/U-brannerite
- ~ 5 - 10 vol. % ThO<sub>2</sub>
- ~ 3 vol. % Hf-doped rutile
- ~ 1 – 2 vol. % UO<sub>2</sub>

This sample has a porous microstructure and the composition of the phases was variable across the pellet, indicating incomplete milling. The inefficient milling has resulted in residual unreacted ThO<sub>2</sub> and UO<sub>2</sub>.

##### 4.2.3.1.4 B1-10 Oxide wet-mill 16 hours

*Sample mws980145* (Appendix E, Table E-2 and Figure E-4) – This sample consisted of:

- pyrochlore
- ~ 30 - 40 vol. % 2M zirconolite

- ~ 20 vol. % Th/U-brannerite
- < 1 vol. % UO<sub>2</sub>
- < 1 vol. % ThO<sub>2</sub>

The oxide-route wet-mill sample had a porous microstructure. Small spots (< 1 μm diameter) of unreacted ThO<sub>2</sub> (< 1 vol. %) were detected within the Th/U-brannerite grains. A small amount of reacted UO<sub>2</sub>, which contains Ca, Gd, Hf and Ti, was also found in the matrix. One 4 μm grain of unreacted hafnia was also detected; presumably, this comes from an agglomerate in the raw material. The Th/U-brannerite is much finer (~ 1 – 5 μm) than in the dry-milled sample (section 4.2.3.1.4). No rutile was detected.

#### **4.2.3.2 Composition B1-10 alkoxide-route sintered at 1300°C in Ar for 4 hours**

*Sample mws980311* (Appendix E, Table E-3 and Figure E-5) – This sample consisted of:

- pyrochlore
- ~30 – 40 vol. % 2M zirconolite
- ~ 20 – 30 vol. % Th/U-brannerite.

The composition of the Th/U-brannerite is variable across the pellet. The microstructure is similar, but finer than that of the pellet sintered at 1350°C in Ar (section 4.2.3.1.2).

#### **4.2.3.3 Composition B1-10 alkoxide route sintered at 1400°C in Ar for 4 hours**

*Sample mws980325* (Appendix E, Table E-3 and Figure E-6) – This sample consisted of:

- ~ 40 vol. % pyrochlore
- ~ 40 vol. % 2M zirconolite
- ~ 20 vol. % Th/U-brannerite

The microstructure (fig. 10) is similar to, but coarser than that of the pellet sintered at 1350°C in Ar (section 4.2.3.1.2).

#### **4.2.3.4 Composition B1-10 oxide route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours**

*Sample mws980409* (Appendix E, Table E-4 and Figure E-7) – This sample consisted of:

- ~ 30 - 40 vol. % pyrochlore
- ~ 40 vol. % 2M zirconolite
- ~ 20 - 30 vol. % Th/U-brannerite
- << 1 vol. % (Th,U)O<sub>2</sub>

The microstructure (fig. 10) is similar to, but coarser than that of the pellet sintered at 1350°C in Ar (section 4.2.3.1.2).

#### **4.2.3.5 Composition B1-10 alkoxide-route sintered at 1350°C in Ar for 75 hours**

*Sample mws980349* (Appendix E, Table E-3 and Figure E-8) – This sample consisted of:

- ~ 40 vol. % pyrochlore
- ~ 40 vol. % 2M zirconolite
- ~ 20 vol. % Th/U-brannerite

The microstructure is less porous to that of the pellet sintered at 1350°C for 4 hours in Ar (section 4.2.3.1.4) and the grain size is coarser.

#### **4.2.3.6 Composition B1-10 oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours**

*Sample mws980395* (Appendix E, Table E-4 and Figure E-9) – This sample consisted of:

- ~ 40 vol. % pyrochlore
- ~ 40 vol. % 2M zirconolite
- ~ 20 vol. % Th/U-brannerite
- << 1 vol. % (Th,U)O<sub>2</sub>

The microstructure is similar to that of the pellet sintered at 1350°C for 4 hours in Ar (section 4.2.3.1.4), but coarser and less porous.

#### **4.2.4 Composition B1-12 – Brannerite-rich**

The XRD results on samples made from composition B1-2 are given in Appendix B and SEM micrographs and EDS results are given in Appendix F.

The brannerite-rich samples consist of an approximately equal mixture of brannerite and pyrochlore with any minor phases, e.g., rutile, dispersed throughout this matrix.

##### **4.2.4.1 Composition B1-12 sintered at 1350°C in Ar for 4 hours**

###### **4.2.4.1.1 B 1-12 Alkoxide wet-mill 4 hours**

*Sample mws980110* (Appendix F, Table F-1 and Figure F-1) – This sample consisted of:

- pyrochlore
- ~ 40 - 50 vol. % Th/U-brannerite
- < 1 vol. % Hf-doped rutile

The composition of the phases was variable across the pellet indicating incomplete milling.

###### **4.2.4.1.2 B1-12 Alkoxide wet-mill 16 hours**

*Sample mws980179* (Appendix F, Table F-1 and Figure F-2) – This sample consisted of:

- pyrochlore
- ~ 40 - 50 vol. % Th/U-brannerite

The pellets made from the 16 hour milled powder had a similar microstructure to that of the 4 hour mill batch (preceding section)

###### **4.2.4.1.3 B1-12 Oxide dry-mill 16 hours**

*Sample mws980143* (Appendix F, Table F-2 and Figure F-3) – This sample consisted of:

- pyrochlore
- ~ 30 - 40 vol. % Th/U-brannerite
- ~ 10 vol. % Hf-doped rutile
- ~ 7 – 10 vol. % of “unreacted” ThO<sub>2</sub>
- ~ 5 vol. % 2M zirconolite

- < 1 vol % fine “reacted” UO<sub>2</sub>
- << 1 vol. % whitlockite<sup>10</sup>

The composition of the phases was variable across the pellet indicating incomplete milling. The pellet made from this powder was porous and had a coarse microstructure with Th/U-brannerite grains up to about 20 – 60 μm across, which contained a large core of unreacted ThO<sub>2</sub>. In some cases, the ThO<sub>2</sub> occupied about 50-70 % of the brannerite grain. The rest of the material consisted of pyrochlore with some 2M zirconolite and Hf-doped rutile. Some UO<sub>2</sub> was detected, which contained Ca, Gd, Hf and Ti, indicating that the UO<sub>2</sub> had partly reacted during sintering. The powder clearly needs more milling before sintering.

#### **4.2.4.1.4 B1-12 Oxide wet-mill 16 hours**

*Sample mws980141* (Appendix F, Table F-2 and Figure F-4) – This sample consisted of:

- pyrochlore
- ~ 30 - 40 vol. % Th/U-brannerite
- ~ 3 - 5 vol. % Hf-doped rutile
- ~ 2 - 5 vol. % 2M zirconolite
- < 1 vol. % fine (Th,U)O<sub>2</sub>
- << 1 vol. % whitlockite<sup>10</sup>

Oxide-route wet-mill – pellets made from this batch had a similar microstructure to the alkoxide-route, 16 hour mill sample (section 4.2.4.1.2), except that they contained a small amount of 2M zirconolite, Hf-doped rutile, phosphate-bearing phase (probably whitlockite), UO<sub>2</sub> and ThO<sub>2</sub>.

#### **4.2.4.2 Composition B1-12 alkoxide-route sintered at 1300°C in Ar for 4 hours**

*Sample mws980313* (Appendix F, Table F-3 and Figure F-5) – This sample consisted of:

- pyrochlore
- ~ 30 - 40 vol. % Th/U-brannerite
- ~ 2- 3 vol. % 2M or 4M zirconolite

The microstructure is similar, but finer than that of the pellet sintered at 1350°C in Ar (section 4.2.4.1.2). The composition of the Th/U-brannerite is similar to that of the 1350°C sample.

#### **4.2.4.3 Composition B1-12 alkoxide-route sintered at 1400°C in Ar for 4 hours**

*Sample mws980326* (Appendix F, Table F-3 and Figure F-6) – This sample consisted of:

- ~ 50 vol. % pyrochlore
- ~ 50 vol. % Th/U-brannerite

The microstructure is similar, but coarser than that of the pellet sintered at 1350°C in Ar (section 4.2.4.1.2). The pellet is very porous.

#### **4.2.4.4 Composition B1-12 oxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours**

*Sample mws980410* (Appendix F, Table F-4 and Figure F-7) – This sample consisted of:

- ~ 50 vol. % pyrochlore
- ~ 50 vol. % Th/U-brannerite

- 1 – 2 vol. % rutile
- < 1 vol. % (Th,U)O<sub>2</sub>, located inside the brannerite

The microstructure is similar, but coarser than that of the pellet sintered at 1350°C in Ar (section 4.2.4.1.4). The pellet is has considerably less porosity than the alkoxide-route sample (section 4.2.4.3).

#### **4.2.4.5 Composition B1-12 sintered at 1350°C in Ar for 75 hours**

*Sample mws980350* (Appendix F, Table F-3 and Figure F-8) – This sample consisted of:

- pyrochlore
- ~ 45 - 50 vol. % Th/U-brannerite
- < 1 vol. % Hf-doped rutile

The microstructure is coarser than that of the alkoxide-route pellet sintered at 1350°C for 4 hours in Ar (section 4.2.4.1.2). The pellet is very porous.

#### **4.2.4.6 Composition B1-12 oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours**

*Sample mws980396* (Appendix F, Table F-4 and Figure F-9) – This sample consisted of:

- pyrochlore
- ~ 45 - 55 vol. % Th/U-brannerite
- ~ 2 - 3 vol. % Hf-doped rutile

The microstructure is coarser than that of the oxide-route pellet sintered at 1350°C for 4 hours in Ar (section 4.2.4.1.4).

### **4.2.5 Composition B1-14 – nominally ~ 10 % Perovskite Doped**

#### **4.2.5.1 Composition B1-14 sintered at 1350°C in Ar for 4 hours**

Despite the formulation having a nominal perovskite composition of ~ 10 %, perovskite (~ 7 vol. %) was only detected in the inhomogeneous dry-milled batch sintered in Ar. In this particular batch a large amount of the Th was present as unreacted thoria, which results in excess Ca and Ti in the matrix, which in turn react to form perovskite. No perovskite was detected in the wet-milled batches sintered in Ar or air.

##### **4.2.5.1.1 B1-14 Alkoxide wet-mill 16 hours**

*Sample mws980262* (Appendix G, Table G-1 and Figure G-1) – This sample consisted of:

- pyrochlore
- ~ 5 vol. % Th/U-brannerite
- ~ 1 vol. % ThO<sub>2</sub> located within the Th/U-brannerite grains
- ~ 1 vol. % Hf-doped rutile

There is no perovskite in the material. The additional Ca, compared to the baseline has been incorporated into the pyrochlore with the Ca content approaching one formula unit. The Th/U-brannerite composition is variable from grain to grain. The Th content is higher in this Th/U-brannerite than that in the baseline ceramic. The sample is porous.

#### **4.2.5.1.2 B1-14 Oxide dry-mill 16 hours**

*Sample mws980283* (Appendix G, Table G-1 and Figure G-2) – This sample consisted of:

- Pyrochlore
- ~ 20 vol. % 2M zirconolite
- ~ 7 vol. % perovskite
- ~ 5 - 10 vol. % Th/U-brannerite
- ~ 5 vol. % ThO<sub>2</sub> located within the Th/U-brannerite grains
- ~ 1 vol. % of UO<sub>2</sub>, which may contain some Th

The pellet is inhomogeneous; milling is insufficient. This inhomogeneity has led to the formation of perovskite, due to the low reactivity of the large thoria grains. In samples where the thoria had reacted, no perovskite was detected (see, e.g., alkoxide-route sample section 4.2.5.1.1 above).

#### **4.2.5.1.3 B1-14 Oxide wet-mill 16 hours**

*Sample mws980258* (Appendix G, Table G-1 and Figure G-3) – This sample consisted of:

- pyrochlore
- ~ 5 - 7 vol. % Hf-doped rutile
- << 1 vol. % whitlockite<sup>10</sup>

The sample is similar to the alkoxide-route sample (section 4.2.5.1.1).

#### **4.2.5.2 Composition B1-14 sintered at 1350°C in air for 4 hours**

The XRD results on samples made from composition B1-2 are given in Appendix B and SEM micrographs and EDS results are given in Appendix G.

##### **4.2.5.2.1 B1-14 Alkoxide wet-mill 16 hours**

*Sample mws980268* (Appendix G, Table G-2 and Figure G-4) – This sample consisted of:

- pyrochlore
- ~ 7 vol. % Th/U-brannerite
- ~ 1 vol. % ThO<sub>2</sub> located within the Th/U-brannerite grains
- < 1 vol. % Hf-doped rutile

The pellet is similar to the pellet fired in Ar (section 4.2.5.1.1), except that it has coarser grains. The pyrochlore contains slightly more Ca than the Ar atmosphere pellet. The Th/U-brannerite composition is variable from grain to grain and similar to that of the Ar sintered pellet above. No perovskite was present.

##### **4.2.5.2.2 B1-14 Oxide dry-mill 16 hours**

*Sample mws980288* (Appendix G, Table G-2 and Figure G-5) – This sample consisted of:

- pyrochlore
- ~ 10 - 15 vol. % 2M zirconolite
- ~ 10 vol. % Th/U-brannerite
- ~ 3 – 5 vol. % ThO<sub>2</sub> located within the Th/U-brannerite grains
- ~ 1 – 3 vol. % Hf-doped rutile

The pellet is inhomogeneous and is similar to the Ar fired sample (section 4.2.5.1.2). No perovskite was detected.

#### **4.2.5.2.3 B1-14 Oxide wet-mill 16 hours**

*Sample mws980286* (Appendix G, Table G-2 and Figure G-6) – These samples consisted of:

- pyrochlore
- ~ 10 vol. % Th/U-brannerite
- ~ 10 vol. % Hf-doped rutile
- < 1 vol. % ThO<sub>2</sub> in the Th/U brannerite grains

The sample is similar to the Ar fired sample (section 4.2.5.1.3). No perovskite was detected.

#### **4.2.5.3 Composition B1-14 alkoxide-route sintered at 1300°C in Ar for 4 hours**

*Sample mws980319* (Appendix G, Table G-3 and Figure G-7) – This sample consisted of:

- pyrochlore
- ~ 15 - 20 vol. % Th/U-brannerite
- ~ 2 - 3 vol. % ThO<sub>2</sub> located within the Th/U-brannerite grains
- ~ 1 vol. % Hf-doped rutile

No perovskite was detected in the sample. The pyrochlore, whose composition is ~ Ca<sub>0.99</sub>Gd<sub>0.19</sub>Th<sub>0.21</sub>U<sub>0.37</sub>Hf<sub>0.27</sub>Ti<sub>2.01</sub>O<sub>7</sub>, is enriched in Ca relative to that of the baseline ceramic (section 4.2.1). The pellet fired at 1300°C is similar to the 1350°C fired pellet (section 4.2.5.1.1) except that it has a finer and more porous microstructure.

The brannerite, whose composition is variable, contains the elements usually found in the brannerite, viz. Gd, Hf, U, Th, Ti and a trace of Ca.

#### **4.2.5.4 Composition B1-14 alkoxide-route sintered at 1400°C in Ar for 4 hours**

*Sample mws980305* (Appendix G, Table G-3 and Figure G-8) – This sample consisted of:

- a pyrochlore matrix.
- ~ 15 vol. % Th/U-brannerite.

The pellet sintered at 1400°C is similar to, but coarser than, the pellet sintered at 1350°C (section 4.2.5.1.1). No perovskite was detected. The Th content is higher in the Th/U-brannerite than that in the baseline ceramic.

#### **4.2.5.5 Composition B1-14 oxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours**

*Sample mws980411* (Appendix G, Table G-4 and Figure G-9) – This sample consisted of:

- a pyrochlore matrix.
- ~ 7 vol. % Hf-doped rutile
- ~ 5 vol. % Th/U-brannerite.

No perovskite was detected. The Th content is higher in the Th/U-brannerite than that in the baseline ceramic.

The pellet sintered at 1400°C is similar to the oxide-route pellet sintered at 1350°C for 75 hours in

Ar (section 4.2.5.7). It is also similar, but coarser than the pellet sintered in air at 1350°C for 4 hours. However, it is different to the sample sintered at 1350°C in Ar for 4 hours, in that it contains rutile. The alkoxide-route samples do not form rutile at higher temperatures or longer sintering times. These results indicate that the samples may be very sensitive to minor changes in the redox conditions, temperature, or composition. Further work is needed to clarify these results.

#### **4.2.5.6 Composition B1-14 alkoxide-route sintered at 1350°C in Ar for 75 hours**

*Sample mws980392* (Appendix G, Table G-3 and Figure G-10) – This sample consisted of:

- pyrochlore
- ~ 3 - 7 vol. % Th/U-brannerite

The pellet is similar to, but coarser than, the pellet sintered at 1350°C for 4 hours (section 4.2.5.1.1). No perovskite was detected.

#### **4.2.5.7 Composition B1-14 oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 75 hours**

*Sample mws980397* (Appendix G, Table G-4 and Figure G-11) – This sample consisted of:

- pyrochlore
- ~ 5 vol. % Th/U-brannerite
- ~ 5 – 7 vol. % Hf-doped rutile

The pellet is similar to the pellet sintered at 1350°C for 75 hours. No perovskite was detected.

### **4.2.6 Composition B1-16 - ~ 10 % Phosphate Doped**

The XRD results on samples made from composition B1-2 are given in Appendix B and SEM micrographs and EDS results are given in Appendix H.

The presence of phosphorus in the batch results in whitlockite, nominally  $\text{Ca}_3(\text{PO}_4)_2$ ; but as can be seen in the EDS analyses (Tables in Appendix H) it contains Gd, Hf, U, Th and Ti. About 10 vol. % of whitlockite formed in each pellet.

#### **4.2.6.1.1 B1-16 Alkoxide wet-mill 16 hours**

*Alkoxide-route sample mws980274* (Appendix H, Table H-1 and Figure H-1) – This sample consisted of:

- pyrochlore
- ~ 20 vol. % Th/U-brannerite
- ~ 10 vol. % whitlockite.

The sample is very porous. The added P was not detected in the pyrochlore and was detected in only trace amounts in the Th/U-brannerite. The bulk of the P had formed whitlockite. The whitlockite contains Gd, Ti and traces of Hf, Th and U. Some Si was also detected in the whitlockite in this sample. The composition of the whitlockite grains is slightly variable across the pellet. The whitlockite contains some Th and U and Hf and a significant amount of Gd (Table H-7). Hence, even though a small amount of U and Th enter the whitlockite, significant amounts of neutron absorbers (Hf and Gd) are also present.

The consumption of Ca to form whitlockite has increased brannerite formation. As with previous Task 1.2 samples, the Th/U-brannerite contains Gd, Hf and Ca and is enriched in Th with respect to the bulk composition.

#### **4.2.6.1.2 B1-16 Oxide dry-mill 16 hours**

*Sample mws980272* (Appendix H, Table H-1 and Figure H-2) –The sample is inhomogeneous and contains:

- pyrochlore
- ~ 10 – 20 vol. % 2M zirconolite
- ~ 10 vol. % Th/U-brannerite
- ~ 10 vol. % of whitlockite
- ~ 5-7 vol. % of unreacted ThO<sub>2</sub>-UO<sub>2</sub>.
- ~ 1 – 3 vol. % Hf-doped rutile
- < 1 vol. % HfO<sub>2</sub>

The composition of the brannerite and ThO<sub>2</sub>-UO<sub>2</sub> is variable across the sample. The ThO<sub>2</sub>-UO<sub>2</sub> is located inside Th/U-brannerite grains. Some of the Th/U-brannerite is up to ~ 20 µm across. The presence of unreacted ThO<sub>2</sub>-UO<sub>2</sub> has led to an excess of Hf in some regions with the resulting formation of 2M zirconolite. Some 4M zirconolite may also be present but the grains are too small to analyse. A large ~ 5 µm grain of hafnia was also detected. The dry-milling was clearly insufficient.

#### **4.2.6.1.3 B1-16 Oxide wet-mill 16 hours**

*Sample mws980270* (Appendix H, Table H-1 and Figure H-3) –The sample consists of:

- pyrochlore
- ~ 15 vol. % Th/U-brannerite
- ~ 10 vol. % of whitlockite
- < 1 vol. % of unreacted ThO<sub>2</sub>-UO<sub>2</sub>

The sample is similar to the alkoxide-route sample (section 4.2.6.1.1) but is less porous and contains some ThO<sub>2</sub>-UO<sub>2</sub> regions that are < 1 µm across and are located inside Th/U-brannerite grains.

### **4.2.6.2 Composition B1-16 sintered at 1350°C in air for 4 hours**

#### **4.2.6.2.1 B1-16 Alkoxide wet-mill 16 hours**

*Alkoxide-route sample mws980280* (Appendix H, Table H-2 and Figure H-4) – This sample consisted of:

- pyrochlore
- ~ 20 - 30 vol. % Th/U-brannerite
- ~ 10 vol. % whitlockite.

This sample is less porous than the alkoxide-route sample fired in Ar (section 4.2.6.1.1). It appears to have slightly more brannerite.

#### 4.2.6.2.2 B1-16 Oxide dry-mill 16 hours

*Sample mws980278* (Appendix H, Table H-2 and Figure H-5) –The sample is extremely inhomogeneous, too inhomogeneous for quantitative analysis and contains:

- pyrochlore
- 2M zirconolite
- hafnium titanate
- Th/U-brannerite
- whitlockite
- ThO<sub>2</sub>
- UO<sub>2</sub>.
- TiO<sub>2</sub>

The sample is porous and consists of large (up to 500 μm) aggregates of variable composition. Significant amounts of unreacted ThO<sub>2</sub>, UO<sub>2</sub> and rutile are present.

#### 4.2.6.2.3 B1-16 Oxide wet-mill 16 hours

*Sample mws980276* (Appendix H, Table H-2 and Figure H-6) –The sample consists of:

- pyrochlore
- ~ 25-30 vol. % Th/U-brannerite
- ~ 10 vol. % of whitlockite

This sample is very similar to the alkoxide-route sample (section 4.2.6.2.1).

#### 4.2.6.3 Composition B1-16 alkoxide-route sintered at 1300°C in Ar for 4 hours

*Sample mws980321* (Appendix H, Table H-3 and Figure H-7) – This sample consisted of:

- ~ 65 - 70 vol. % pyrochlore
- ~ 20 - 25 vol. % Th/U-brannerite
- ~ 10 vol. % whitlockite (nominally, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>). This phase is fine-grained (~ 0.5 μm) with composition of ~ Ca<sub>2.21</sub>Gd<sub>0.17</sub>Hf<sub>0.16</sub>U<sub>0.12</sub>Th<sub>0.09</sub>Ti<sub>0.52</sub>P<sub>1.6</sub>O<sub>8</sub>.

The pellet sintered at 1300°C is similar to the 1350°C and 1400°C samples (sections 4.2.6.1.1 and 4.2.6.4) but has a finer grain size. The phases present, their amounts and compositions are also similar to the 1400°C sintered pellet.

#### 4.2.6.4 Composition B1-16 alkoxide-route sintered at 1400°C in Ar for 4 hours

*Sample mws980307* (Appendix H, Table H-3 and Figure H-8) – This sample consisted of:

- pyrochlore
- ~ 20 vol. % Th/U-brannerite.
- ~ 10 vol % whitlockite

The sample is similar in phase distribution to the 1300 and 1350°C samples (sections 4.2.6.1.1 and 4.2.6.3); however, the microstructure is coarser and the pores have closed.

#### 4.2.6.5 Composition B1-16 oxide-route, wet-milled 16 hours, sintered at 1400°C in Ar for 4 hours

*Sample mws980412* (Appendix H, Table H-4 and Figure H-9) – This sample consisted of:

- pyrochlore
- ~ 15 – 20 vol. % Th/U-brannerite.
- ~ 10 vol % whitlockite
- < 1 vol. % (Th,U)O<sub>2</sub>, located inside the brannerite grains

The sample is similar in phase distribution to the 1350°C sample (sections 4.2.6.1.3), except that the microstructure is coarser.

#### **4.2.6.6 Composition B1-16 alkoxide-route sintered at 1350°C in Ar for 75 hours**

*Sample mws980393* (Appendix H, Table H-3 and Figure H-10) – This sample consisted of:

- pyrochlore
- ~ 20 vol. % Th/U-brannerite
- ~ 10 vol % whitlockite

The sample microstructure is coarser than that of the 1350°C/4 hour sample (section 4.2.6.1.1), however the phases present are similar.

#### **4.2.6.7 Composition B1-16 oxide-route, wet-milled 16 hours sintered at 1350°C in Ar for 75 hours**

*Sample mws980398* (Appendix H, Table H-4 and Figure H-11) – This sample consisted of:

- pyrochlore
- ~ 20 vol. % Th/U-brannerite.
- ~ 10 vol % whitlockite
- ~ 0.5 vol % UO<sub>2</sub> as fine grains located within the Th/U-brannerite grains

The sample microstructure is less porous than that of the 1350°C/4 hour sample (section 4.2.6.1.3). The additional sintering time has aided densification.

### **4.3 Pu/U-doped Samples**

Note that compositions B1-1, oxide-route wet and dry-milled, and B1-3 alkoxide-route, have already been examined in 1997<sup>1</sup>. Only an alkoxide-route batch of B1-1 has been made in the present work. New pellets have however been made from the B1-1 composition wet-milled oxide-route powder (Pu-68) and composition II-7A made in 1997<sup>1</sup> for use in section 2.1 of the Task 2. These pellets will be used to examine the effects of surface preparation on leach discs (see the Task 2 October-November progress report for SEM and XRD results on these samples). The microstructural results on these pellets are reported in this section.

#### **4.3.1 Composition B1-1 – Baseline Ceramic**

##### **4.3.1.1 Pu/U-doped composition B1-1 alkoxide-route sintered at 1350°C for 4 hours in Ar**

*Sample mws980293 (Pu92-01A)* (Appendix I, Table I-1 and Figure I-1) – This sample consisted of:

- pyrochlore
- ~ 15 vol % Pu/U-brannerite
- ~ 5 vol. % Hf-doped rutile ( $\sim\text{Hf}_{0.08}\text{Ti}_{0.91}\text{O}_2$ ), which may also contain some U (~ 1.7 wt. %) and a trace of Pu.

The pellet is of similar phase composition to the oxide-route materials made in 1997<sup>1</sup>, but the microstructure is more porous. The sample is also similar to the Th/U-doped baseline ceramic (section 4.2.1.1.2).

#### **4.3.1.2 Pu/U-doped composition B1-1 oxide-route dry-milled 16 hours, sintered at 1350°C for 4 hours in Ar**

This batch was made and discussed in a 1997 report<sup>1</sup>. The results are given here to aid the reader.

*Sample Pu67* (Appendix I, Table I-1 and Figure I-2) – This sample consisted of:

- pyrochlore
- ~ 15 vol % Pu/U-brannerite
- ~ 5 vol. % Hf-doped rutile
- ~ 1 vol. % (Pu,U)O<sub>2</sub>, located within the brannerite grains

The grains in this sample are coarser than the alkoxide-route or wet-milled samples (sections 4.3.1.1 and 4.3.1.3). There is incomplete reaction of the (Pu,U)O<sub>2</sub> and a substantial amount remains – associated with the brannerite.

#### **4.3.1.3 Pu/U-doped composition B1-1 oxide-route wet-milled 16 hours, sintered at 1350°C for 4 hours in Ar**

This batch was made and discussed in a 1997 report<sup>1</sup>. The results here are from a new batch of pellets made for Task 2.1 leach testing.

*Sample mws980199 (Pu68)* (Appendix I, Table I-1 and Figure I-3) – This sample consisted of:

- pyrochlore
- ~ 15 vol % Pu/U-brannerite
- ~ 5 vol. % Hf-doped rutile
- < 1 vol. % (Pu,U)O<sub>2</sub>, located within the brannerite grains

The microstructure is less porous than the alkoxide-route and is more uniform than the dry-milled sample with < 1 vol. % unreacted. There is no difference between this sample and that made in 1997.

### **4.3.2 Composition B1-3 and other Impurity-doped Compositions**

#### **4.3.2.1 Pu/U-doped composition B1-3 alkoxide-route sintered at 1300°C for 4 hours in Ar**

This batch was made and discussed in a 1997 report<sup>1</sup>. The results are given here to aid the reader.

*Sample Pu73* (Appendix I, Table I-2 and Figure I-4) – This sample consisted of:

- pyrochlore
- ~ 10 vol. % Th/U-brannerite

- ~ 7 - 10 vol. % 2M zirconolite
- ~ 3 vol. % Hf-doped rutile
- ~ 1 - 2 vol. % of a silicate phase (Si-Ca-Mg-Na-K-Ti-Al-Ga-O), probably a glass

The sample is similar to the Th/U-doped samples (section 4.2.2.1). The addition of impurities had aided sintering, probably due to glass formation with subsequent liquid-phase sintering.

#### **4.3.2.2 Pu/U-doped composition A-7 wet-milled oxide-route, sintered at 1325°C for 4 hours in Ar**

*Sample mws980200 (Pu75)* (Appendix I, Table I-2 and Figure I-5) – This sample consisted of:

- pyrochlore
- ~ 10 vol. % Th/U-brannerite
- ~ 10 vol. % 2M zirconolite
- ~ 5 - 7 vol. % Hf-doped rutile
- ~ 1 - 2 vol. % of a silicate phase (Si-Ca-Mg-Na-K-Ti-Al-Ga-O), probably a glass
- < 1 vol. % (Pu,U)O<sub>2</sub>, located within the brannerite grains

This sample was made for leach testing in Task 2.1, and is similar to, but less porous than, the alkoxide-route sample made in 1997<sup>1</sup>. It is also similar to the sample made from the same powder in 1997<sup>1</sup>. The sample is also similar to the B1-3 composition samples except that it has slightly more rutile.

An additional batch made from composition B3-13 has been made for leaching studies of impurities. This composition is a modified form of A-7 and contains more elements. Results on this batch will be reported when they become available.

### **4.3.3 Composition B1-9 – Zirconolite-rich**

#### **4.3.3.1 Pu/U-doped composition B1-9 alkoxide-route sintered at 1350°C for 4 hours in Ar**

*Sample mws980294 (Pu93-01A)* (Appendix I, Table I-3 and Figure I-6) – This sample consisted of:

- pyrochlore
- ~ 40 vol. % of 2 M zirconolite
- ~ 20 vol. % Pu/U-brannerite
- ~ 3 vol. % Hf-doped rutile

The sample is similar to the Th/U-doped sample (section 4.2.3.1.2) but slightly more porous.

#### **4.3.3.2 Pu/U-doped composition B1-9 oxide-route, dry-milled 16 hours, sintered at 1350°C for 4 hours in Ar**

*Sample mws9800353 (Pu098-01A)* (Appendix I, Table I-3 and Figure I-7) – This sample consisted of:

- pyrochlore
- ~ 30 - 40 vol. % of 2 M zirconolite

- ~ 10 – 15 vol. % Pu/U-brannerite
- ~ 3 - 5 vol. % Hf-doped rutile
- ~ 1 vol. % PuO<sub>2</sub>

The sample is more homogeneous than the Th/U-doped sample (section 4.2.3.1.3); indicating that the milling or sintering was more complete. Reasons for this are discussed in section 4.5 below.

The sample has a coarser grain size than the wet-milled (section 4.3.3.3) or alkoxide-route samples (section 4.3.3.1). The sample contains more unreacted PuO<sub>2</sub> than either of these batches.

#### **4.3.3.3 Pu/U-doped composition B1-9 oxide-route, wet-milled 16 hours, sintered at 1350°C for 4 hours in Ar**

*Sample mws9800352 (Pu097-01A)* (Appendix I, Table I-3 and Figure I-8) – This sample consisted of:

- pyrochlore
- ~ 40 vol. % of 2M zirconolite
- ~ 10 vol. % Pu/U-brannerite
- ~ 3 - 5 vol. % Hf-doped rutile
- < 1 vol. % PuO<sub>2</sub>

The sample is less porous than the Th/U-doped sample (section 4.2.3.1.4). The sample has less porosity than the alkoxide-route samples (section 4.3.3.1). The sample contains some unreacted PuO<sub>2</sub>.

#### **4.3.4 Composition B1-11 – brannerite-rich**

##### **4.3.4.1 Pu/U-doped composition B1-11 alkoxide-route sintered at 1350°C for 4 hours in Ar**

*Sample mws980295 (Pu94-01A)* (Appendix I, Table I-4 and Figure I-9) – This sample consisted of:

- pyrochlore
- 40 – 50 vol. % Pu/U-brannerite
- ~ 2 vol. % reacted (U,Pu)O<sub>2</sub>

There is a significant amount of (U,Pu)O<sub>2</sub> that contains Ca, Gd, Hf and Ti.

##### **4.3.4.2 Pu/U-doped composition B1-11 oxide-route, dry-milled, sintered at 1350°C for 4 hours in Ar**

*Sample mws980355 (Pu100-01A)* (Appendix I, Table I-4 and Figure I-10) – This sample consisted of:

- pyrochlore
- ~ 50 vol. % Pu/U-brannerite
- ~ 3 – 5 vol. % Hf-doped rutile
- < 1 vol. % (U,Pu)O<sub>2</sub>

As with most dry-milled samples, there is some unreacted PuO<sub>2</sub>. The sample is much more uniform than the dry-milled Th/U-doped sample (section 4.2.4.1.3); reasons for this will be

discussed below. The sample is similar to the wet-milled sample (section 4.3.4.3)

#### **4.3.4.3 Pu/U-doped composition B1-11 oxide-route, wet-milled 16 hours, sintered at 1350°C for 4 hours in Ar**

*Sample mws980354 (Pu099-01A)* (Appendix I, Table I-3 and Figure I-11) – This sample consisted of:

- pyrochlore
- ~ 50 vol. % Pu/U-brannerite
- ~ 3 – 5 vol. % Hf-doped rutile

The sample is very similar to the Th/U-doped sample (section 4.2.4.1.4). Free PuO<sub>2</sub> was not detected. Apart from the free PuO<sub>2</sub>, the sample is similar to the dry milled sample (section 4.3.4.2)

#### **4.3.5 Composition B1-13 – “nominally” 10 % perovskite**

None of the nominally 10 % perovskite samples prepared contained perovskite. The additional Ca is taken up by the pyrochlore with the amount of Ca in the Ca site approaching one formula unit. The samples are different to the Th/U-doped samples (section 4.2.5) in that the major phases formed were pyrochlore and rutile, with no brannerite - in the Th/U-doped samples brannerite had a greater tendency to form. This is probably a reflection of Th having a greater tendency to form brannerite than Pu. It is reflected in the EDS results, which show that Th is enriched in the brannerite with respect to the bulk composition. It also reflects the results from the Task 1.1 (single-phase) work, where thorutite (Th-brannerite) readily formed, whereas Pu-brannerite was more difficult to make.

##### **4.3.5.1 Pu/U-doped composition B1-13 alkoxide-route sintered at 1350°C for 4 hours in Ar**

*Sample mws980361 (Pu105-01A)* (Appendix I, Table I-5 and Figure I-12) – This sample consisted of:

- pyrochlore
- ~ 3 - 5 vol. % Hf-doped rutile

##### **4.3.5.2 Pu/U-doped composition B1-13 oxide-route, dry-milled, sintered at 1350°C for 4 hours in Ar**

*Sample mws980357 (Pu102-01A)* (Appendix I, Table I-4 and Figure I-13) – This sample consisted of:

- pyrochlore
- ~ 3 - 5 vol. % Hf-doped rutile
- < 1 vol. % (U,Pu)O<sub>2</sub>

The sample is similar to the alkoxide-route sample (section 4.3.5.1) except that it has some lumps of PuO<sub>2</sub> present. The sample is more homogeneous than the Th/U-doped sample (section

4.2.5.1.2); indicating that the milling or sintering was more complete. Reasons for this are discussed in section 4.5 below.

#### **4.3.5.3 Pu/U-doped composition B1-13 oxide-route, wet-milled 16 hours, sintered at 1350°C for 4 hours in Ar**

*Sample mws980356 (Pu101-01A)* (Appendix I, Table I-4 and Figure I-14) – This sample consisted of:

- pyrochlore
- ~ 5 vol. % Hf-doped rutile

The sample is very similar to the alkoxide-route sample (section 4.3.5.1) except that it is less porous.

#### **4.3.6 Composition B1-15 – 10 % phosphate-doped**

The effect of adding phosphate to the batch was to form whitlockite (nominally  $\text{Ca}_3\text{P}_2\text{O}_8$ ). The whitlockite contained traces of Pu, U, Ti, and Hf and significant amounts of Gd. Hence, although some Pu (~ 0.02 formula units) is present in the whitlockite, substantially more neutron absorbers are present (Gd ~ 0.22 formula units) in the phase.

The major phase difference to the Th/U-doped samples is that these Pu/U-doped samples contained ~ 5 vol. % rutile and less brannerite. This may reflect the greater tendency of Th to enter the brannerite, compared to Pu.

##### **4.3.6.1 Pu/U-doped composition B1-15 alkoxide-route sintered at 1350°C for 4 hours in Ar**

*Sample mws980362 (Pu106-01A)* (Appendix I, Table I-5 and Figure I-15) – This sample consisted of:

- pyrochlore
- ~ 10 vol. % Pu/U-brannerite
- ~ 5 - 7 vol % whitlockite
- ~ 5 vol. % Hf-doped rutile

The sample is quite porous, reflected in the low density (Table 6); though most of the porosity is closed (low apparent porosity value for the sample - given in Table 6).

##### **4.3.6.2 Pu/U-doped composition B1-15 oxide-route, dry-milled, sintered at 1350°C for 4 hours in Ar**

*Sample mws980359 (Pu104-01A)* (Appendix I, Table I-5 and Figure I-16) – This sample consisted of:

- pyrochlore
- ~ 10 - 15 vol. % Pu/U-brannerite
- ~ 5 - 7 vol % whitlockite
- ~ 5 vol. % Hf-doped rutile
- < 1 vol. %  $\text{PuO}_2$

The sample is less porous than the alkoxide-route sample (section 4.3.6.1). It has some lumps of

PuO<sub>2</sub> present; indicating that milling was incomplete.

The sample is more homogeneous than the Th/U-doped sample (section 4.2.6.1.2); indicating that the milling or sintering was more complete. Reasons for this are discussed in section 4.5 below.

#### **4.3.6.3 Pu/U-doped composition B1-15 oxide-route, wet-milled 16 hours, sintered at 1350°C for 4 hours in Ar**

*Sample mws980358 (Pu103-01A)* (Appendix I, Table I-5 and Figure I-17) – This sample consisted of:

- pyrochlore
- ~ 10 - 15 vol. % Pu/U-brannerite
- ~ 5 - 7 vol % whitlockite
- ~ 5 – 7 vol. % Hf-doped rutile
- << 1 vol. % PuO<sub>2</sub>.

The sample is less porous than the alkoxide-route sample (section 4.3.6.1). There is a sparse amount of very small (too small to analyse) PuO<sub>2</sub> regions, located inside the brannerite grains.

The sample is more similar to the Th/U-doped sample (section 4.2.6.1.3), except that it has a coarser grain size and is less porous.

## **4.4 Firing in Hydrogen Atmospheres**

Selected samples were fired in 3.7 % H<sub>2</sub> in Ar for 4 hours at 1350°C. The results are given in Appendix J.

- Baseline alkoxide-route (mws980297, Figure J-1 and Table J-1) – The sample had a finer grain size and lower porosity than the 1350°C in Ar sample (section 4.2.1.1.2). The sample consists of a pyrochlore matrix, with about 15 – 20 vol. % of what is believed to be 2M zirconolite and about 10 vol. % perovskite.
- Zirconolite-rich alkoxide-route (mws980299, Figure J-2 and Table J-1) – The sample had a similar grain size and porosity to the 1350°C in Ar sample (section 4.2.3.1.2). The sample consists of an approximately equal mixture of pyrochlore, 4M zirconolite and 2M zirconolite and about 2 - 3 vol. % perovskite.
- Brannerite-rich alkoxide-route (mws980301, Figure J-3 and Table J-1) – The sample was different to the 1350°C in Ar sample (section 4.2.4.1.2). The sample consists of a pyrochlore matrix, with ~ 10 - 15 vol. % of what is believed to be 4M zirconolite, ~ 10 – 15 vol. % brannerite, which exhibits substantial zoning and ~2 – 3 vol. % (Th,U)O<sub>2</sub>.

The EDS results (Table J-1) suggest that there are significant amounts of Ti<sup>3+</sup> in these materials. The charge compensation occurs by reducing the amount of Ca in the Ca site of the pyrochlores. This Ca is presumably replaced by Gd and U. In the baseline and zirconolite-rich batches this has had the effect of promoting perovskite and zirconolite formation. In the brannerite-rich sample, the effect of reducing conditions has been to destabilise the brannerite, with U and Th moving to the pyrochlore at the expense of Hf and Ca and zirconolite forming. (Th,U)O<sub>2</sub> has precipitated out of solution, which probably indicates that the sample is saturated in actinides.

## 5 CONCLUSIONS

### 5.1.1 The Effect of Milling Time and Method

The dry ball milled batches all “caked” badly on milling, although they were pre-dried in the milling jar. After 16 hours milling a hard cake, several mm thick had formed on the nylon jars used for milling the Th/U-doped powders. The Pu/U-doped batches dry-milled better than the Th/U-doped batches to give less heterogeneous powders. The major difference was that the Pu/U-doped batches were milled in a rubber jar, while the Th/U-doped batches were milled in a nylon jar. The flexibility of the rubber jar, which reduced caking, compared to the rigidity of the nylon jar, may explain the difference. However, the media in both milling jars were coated with powder on milling. The only Th-doped dry-milled batch out of the 6 tested that exhibited, what may be considered a satisfactory microstructure was the baseline + impurities batches (B1-4). In this batch the liquid phase formed on sintering, reduced the effect of inhomogeneity in the green pellet.

On firing, the Th/U-doped oxide-route dry-milled pellets had a lower density and higher porosity due to the aggregates and agglomeration in the powder.

Hence, dry ball milling was not effective in producing homogeneous microstructures and full reactivity in this series of samples. It should be possible to improve dry ball milling by the use of additives, but this was beyond the scope of this work.

For wet-milling, increasing the milling time from 4 to 16 hours significantly improved the densities and uniformity of the microstructure. 4 hour milling did not appear to be sufficient to produce full reactivity, unless sintering aids were present, i.e., a batch of compositions B1-3 and B1-4, for example.

Hence, 16 hours was set as the standard time for ball milling the batches and the wet-milled oxide-route and alkoxide-route batches were used for exploration of the effects of sintering time, temperature and atmosphere.

### 5.1.2 Densities and Sintering Observations

Density trends were discussed above (section 4.1). The effect of temperature on density also varies from batch to batch. For the 4 hour sintering times, at the sintering temperatures tested (1300, 1350 and 1400°C), most of the pellets made from the batches reach a maximum density at about 1350°C. Above this temperature pore and grain growth occurs, which lead to a decrease in density. Pore and grain growth also occurs at extended sintering times.

In the samples with the impurity additions, warping of the pellets occurred, due to partial melting, in the 1350°C and 1400°C sinters.

These laboratory scale results indicate that there are optimum firing temperatures and times for the compositions and that this optimum will vary with the composition. The sintering schedule will also be size driven in that large pellets will sinter differently to small pellets due to temperature gradients. More work, as part of Task 3, will need to be done to clearly identify and define

sintering schedules, for given milling-granulation methods, particularly using methods applicable to the envisaged Pu ceramics plant.

The B1-14 and B1-16 samples fired in air were similar to the samples fired in Ar. Samples sintered in Hydrogenous atmospheres were different to those of air or Ar. The reducing conditions promote the formation of zirconolite and perovskite at the expense of pyrochlore and brannerite.

### 5.1.3 Compositions

Generally, the formulations formed the phases expected. The exception was the nominally ~ 10 % perovskite batch, which did not form perovskite (except for the poorly milled Th/U-doped batch and in this case it was due to the Th being held in large ThO<sub>2</sub> grains, which led to an excess of Ca and Ti in the sample). The following considerations apply to the 16 hour wet-milled oxide-route and alkoxide-route batches (i.e., well milled samples):

- The baseline ceramics, essentially formed pyrochlore as the main phase with 10 – 20 vol. % brannerite and 3 – 5 vol. % Hf-doped rutile.
- The baseline + impurities ceramics formed mainly pyrochlore plus ~ 15 vol % 2M zirconolite, ~ 10 – 20 brannerite, 2 - 3 vol. % Hf-doped rutile and ~ 1 - 2 vol. % of an intergranular silicate phase, probably a glass. The impurities lead to grain growth – probably via liquid phase sintering.
- The zirconolite rich ceramics formed an approximately equal mixture of zirconolite and pyrochlore with ~ 15 – 20 vol. % brannerite and sometimes a little (< 5 vol. %) Hf-doped rutile
- The brannerite-rich samples consist of an approximately equal mixture of brannerite and pyrochlore; sometimes ~ 2 – 3 vol. % Hf-doped rutile was present.
- The nominally ~ 10 % perovskite samples had no perovskite, the additional Ca formed pyrochlore with Ca occupation in the Ca site content close to one formula unit. The additional phases formed, to the main pyrochlore phase, depend on whether the sample was Th or Pu-doped. For Th-doped batches, 5 - 20 vol. % brannerite and 5 – 10 vol. % Hf-doped rutile were present. In the Pu-doped samples ~ 5 vol. % rutile was present.
- The phosphate doped samples typically consisted mainly of pyrochlore with 15 - 20 vol. % brannerite, 5 – 10 vol. % whitlockite and 3 – 7 vol. % Hf-doped rutile. The whitlockite (nominally, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) contains Gd, Hf, U, Th and Ti.

Traces (< 1 vol. %) of ThO<sub>2</sub> and PuO<sub>2</sub> were found in some samples. Sometimes this was “unreacted” and other times it was partly “reacted”. By reacted we mean that it contained significant amounts of the other elements present in the sample (e.g., Ca, Gd, Hf, U, Ti). The term “unreacted” applies, in this work, to lumps of residual material that have not reacted during sintering.

Incomplete milling leads to inhomogeneity in the microstructure. The main effect is that unreacted actinide oxides remain in the microstructure. These are usually surrounded by brannerite. The phase composition also alters due to the actinide being tied up in the oxide, e.g., the pyrochlore has less actinide. In some cases the phase ratios will change, e.g., more brannerite may form. The formation of additional phases can also occur, but these tend to be well characterised phases such as zirconolite (due to insufficient actinide availability leading to an excess of Hf) and in one case

perovskite. If a sintering aids are present, e.g., in the baseline + impurities batch, the effect of processing variables is reduced and the samples are more homogeneous.

The Pu, U and Th partition as expected – mainly into the pyrochlore, brannerite and zirconolite, with some in the whitlockite and rutile. The amounts in the minor phases, rutile and whitlockite, are small however, and the neutron absorbers Hf and Gd can be found in significant amounts in these phases.

### 5.1.4 The Approach to Equilibrium

The approach to equilibrium is determined by a number of factors

- the efficiency of the milling
- the sintering time
- the sintering temperature
- the batch composition.

The latter is very important, e.g., the zirconolite-rich batch has a slower approach to equilibrium than the baseline ceramic requiring higher sintering temperatures or longer sintering times. In addition, the presence of process impurities dramatically alters the approach to equilibrium. The additives produce a silicate liquid phase (at the sintering temperatures), which aids the dissolution and diffusion of the actinide oxide and densification. Even the relatively inhomogeneous dry milled oxide-route samples with processing additives reach 90 – 95 % of their equilibrium state on sintering at 1350°C for 4 hours and the sample with additives fired at 1300°C for 4 hours had only a trace of actinide oxide.

In terms of approach to equilibrium, the following summarises the results for the different batch processing routes. For 4 hours sintering at 1350°C samples:

- dry-milled oxide samples reach ~ 50 – 80 % of their equilibrium state, except for the baseline + additives batch which achieves ~ 90 - 95 % equilibrium
- wet-milled oxide route samples reach ~ 90 – 100 % equilibrium
- alkoxide-route samples reach ~ 95 – 100 % equilibrium

The following refers to alkoxide or wet-milled oxide-routes, dry milled batches were considered too heterogeneous for further study. Sintering for 75 hours at 1350°C gives ~ 98 – 100 % equilibrium. Sintering at 1300°C gives ~ 80 – 95 % equilibrium. Sintering at 1400°C is more difficult to judge as the phase chemistry can change, but generally, the samples sintered for 4 hours at 1400°C are similar to the samples sintered for 75 hours at 1350°C (~ 98 – 100 % equilibrium).

### 5.1.5 Pu-doped Versus Th-doped Samples

The results of the Pu-doped samples are similar to the Th/U-doped batches and produced samples with similar microstructures, which indicate that Th is a good surrogate for Pu in the microstructural context.

The major difference between Th and Pu was that the Th has a greater tendency to form brannerite. For example, In the baseline ceramic the U:Th and U:Pu ratios are 2:1 (in the bulk composition); however, the U:Th ratio in the Th/U-brannerites formed was closer to unity. This results in the Th-doped pyrochlore in the baseline ceramics being slightly deficient in Th (relative the Pu/U-doped ceramics). Similar trends occur in the other compositions. An extreme example of the effect of this

difference between Th and Pu is in the ~ 10 % nominal perovskite batch. In the Th/U-doped batch the phases formed were pyrochlore, Th/U-brannerite, Hf-doped rutile and some (Th,U)O<sub>2</sub> (the latter was only present in the in the oxide-route batches), whereas in the Pu/U-doped batch no brannerite formed. The phases formed in the latter were pyrochlore, Hf-doped rutile and some PuO<sub>2</sub>. The PuO<sub>2</sub>, which usually contains some U, was only present in the oxide-route samples in amounts of < 1 vol. %.