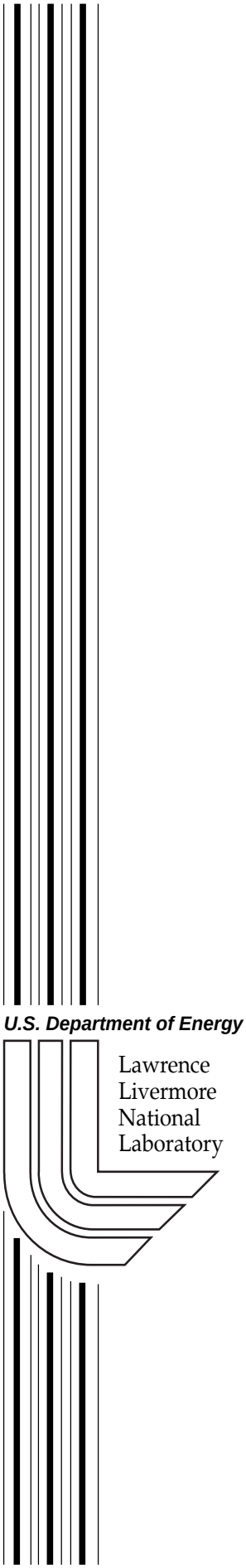
UCRL-CR-139071-PT-2

Interim Report Task 3: Immobilisation Process/Equipment Testing – Task 3.4: Non-Destructive Evaluation Appendices Part 2 of 2 To Lawrence Livermore National Laboratory for Contract B345772



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April 10, 2000

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Interim Report, February 2000, to Lawrence Livermore National Laboratory for Contract B345772 –

Task 3: Immobilisation Process/Equipment Testing – Task 3.4: Non-Destructive Evaluation

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10 April 2000

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Task 3: Immobilisation Process/Equipment Testing –

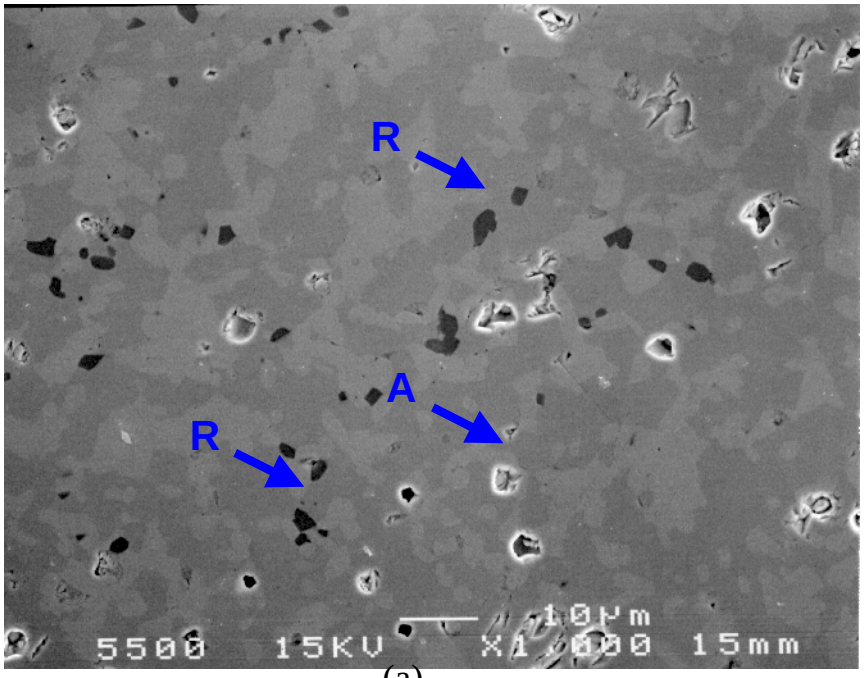
Task 3.4: Non-Destructive Evaluation

APPENDIX A

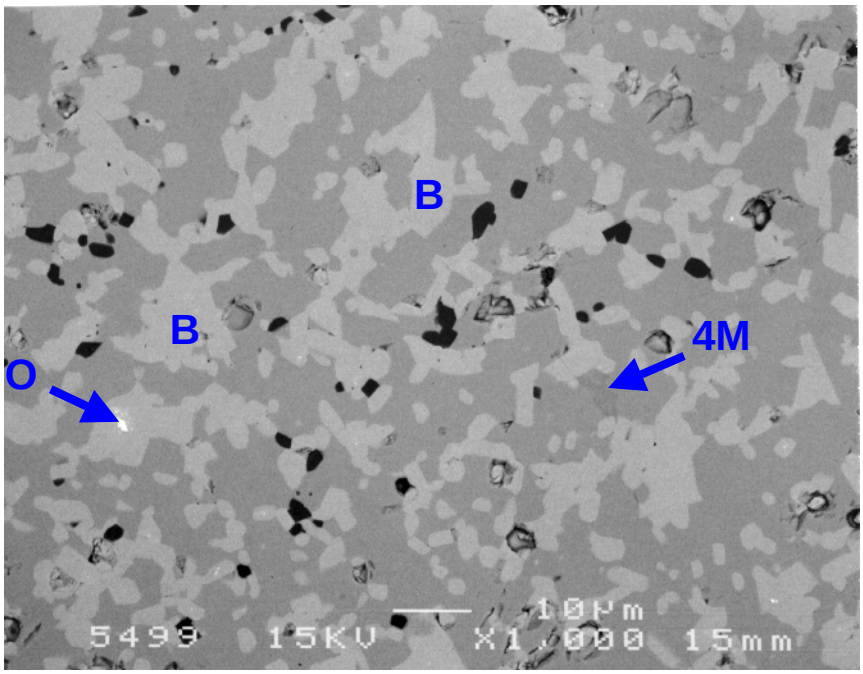
SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-2 - Th/U-DOPED BASELINE CERAMIC

A. APPENDIX A: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-2 - TH/U-DOPED BASELINE CERAMIC

A.1 SEM IMAGES



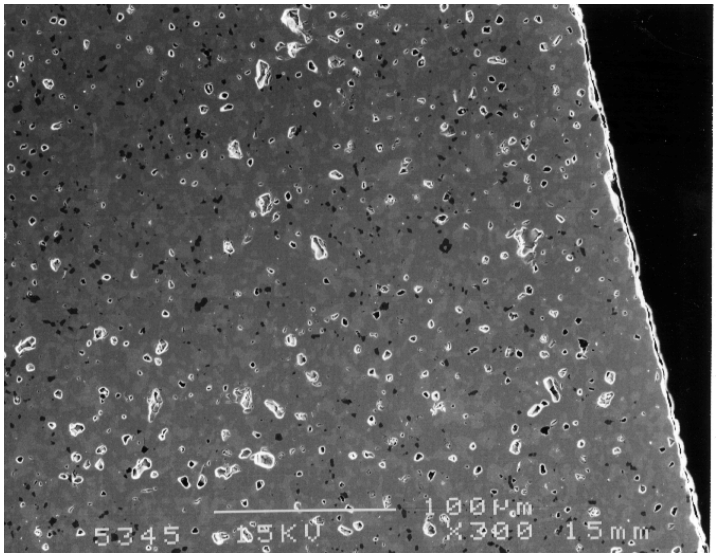
(a)



(b) — 10 µm.

Figure A-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980137 (composition B1-2, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore. Th/U-brannerite (B, light grey grains), Hf-doped rutile (R, dark-grey), 4M zirconolite (4M), ThO_2 (O, white) and porosity (A) are present.

(a)



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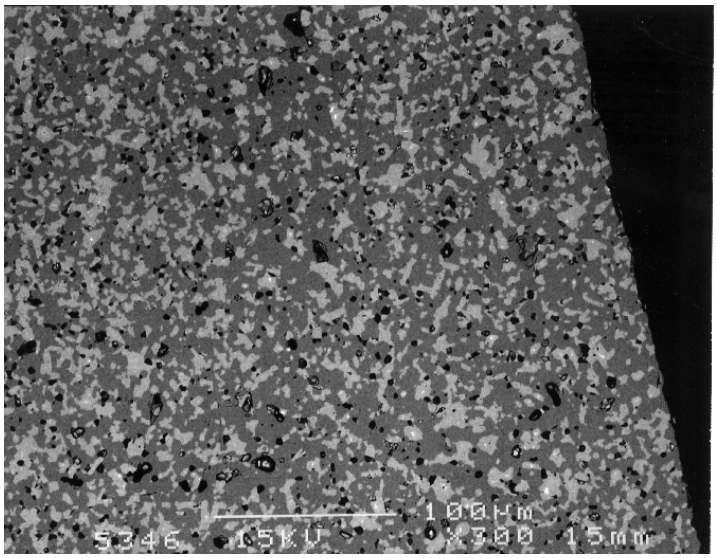

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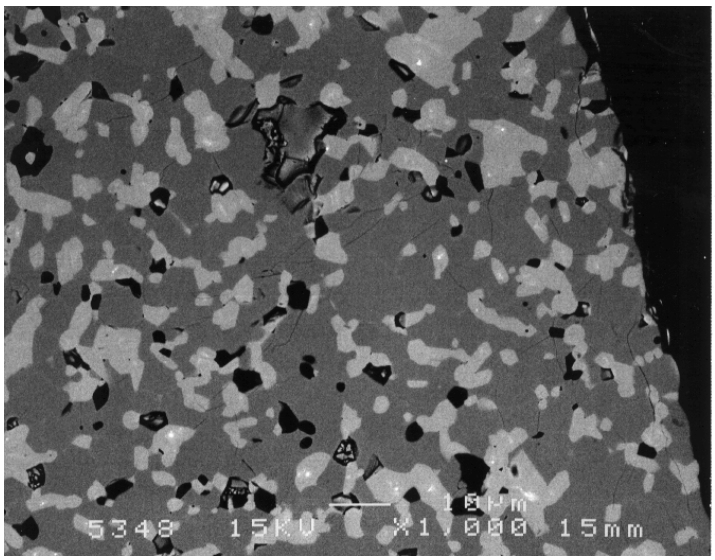
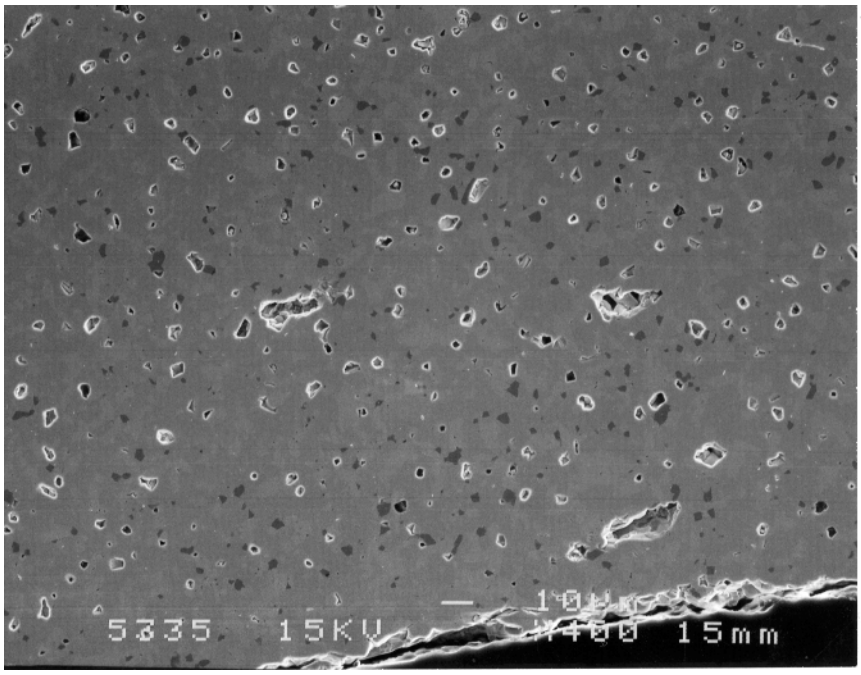
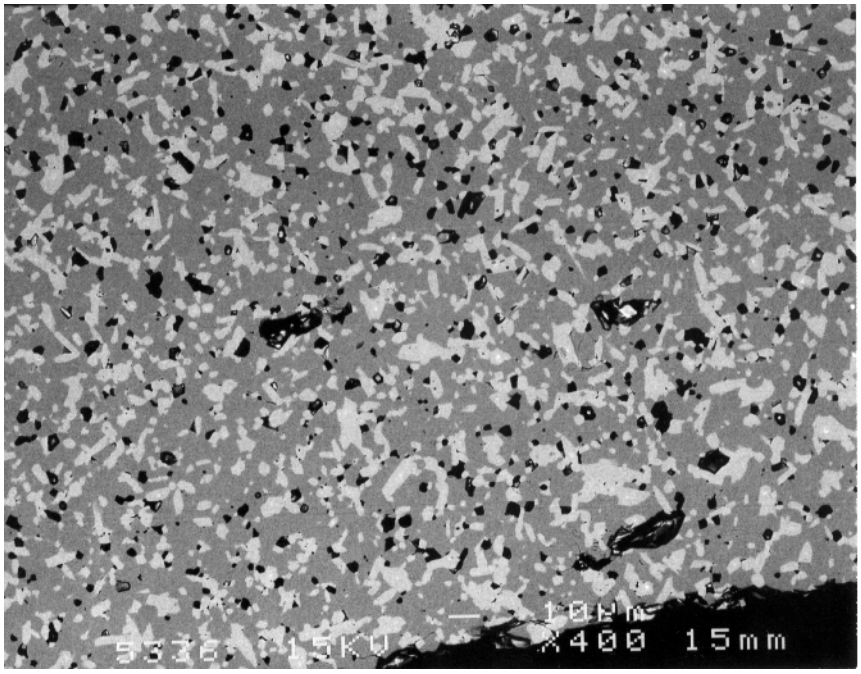


Figure A-2: (a) Secondary electron micrograph and (b) and (c) backscattered electron micrographs of mws990441 (composition B1-2, oxide-route, wet-milled 16 hours, sintered at 1350°C in air for 4 hours). The matrix is pyrochlore. Th/U-brannerite (light grey grains), Hf-doped rutile (dark-grey), ThO_2 (white spots inside brannerite grains) and porosity (see (a)) are also present.

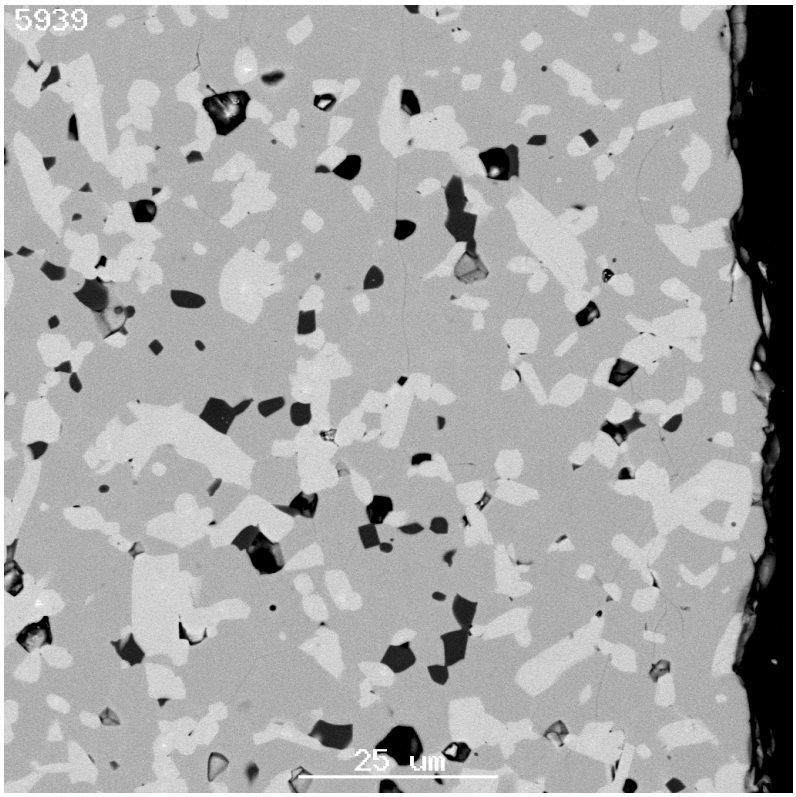


(a)



(b)

Figure A-3: (a) Secondary electron micrograph and, (b), (c) and (d) backscatter electron micrographs of mws99-0527 (composition B1-2, oxide-route, dry-milled, sintered at 1350°C in Ar for 4 hours). Micrograph (c) shows the exterior of the pellet and (d) the interior of the pellet. The matrix is pyrochlore. Th/U-brannerite (grey grains), Hf-doped rutile (dark-grey), ThO_2 (white spots in brannerite grains) and porosity (see (a)) are present.



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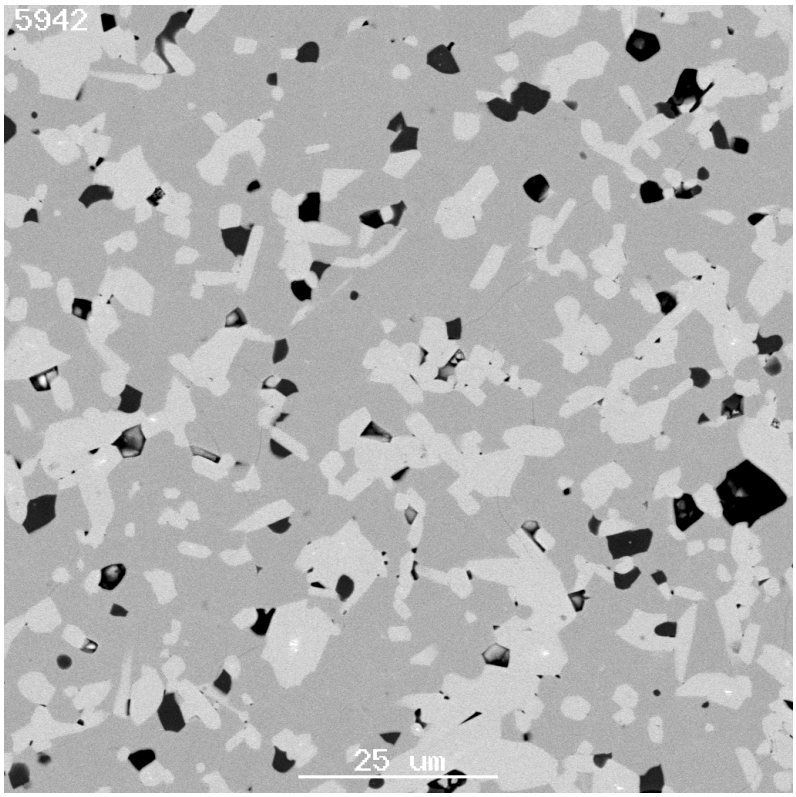


(d)

(a)

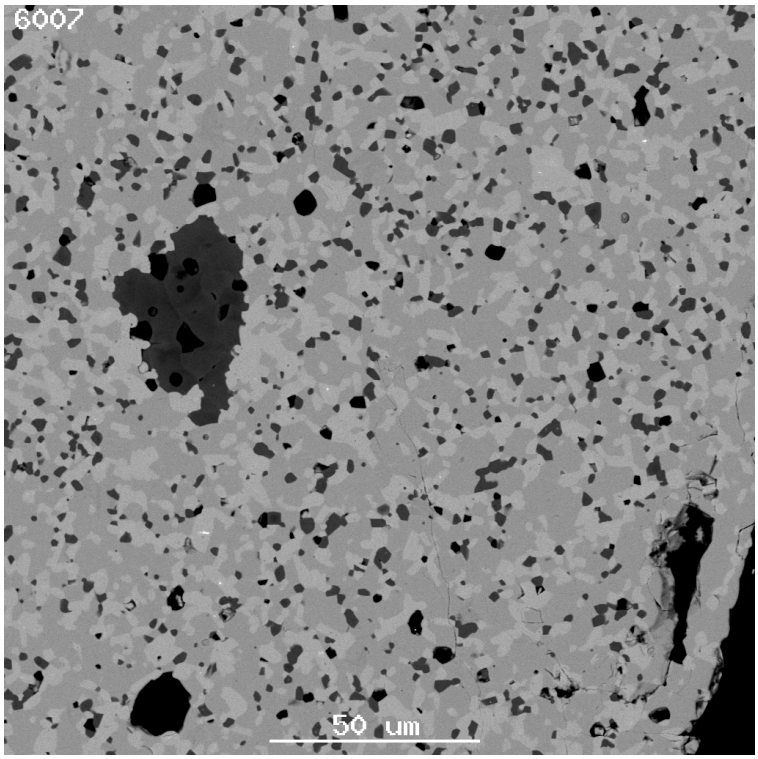
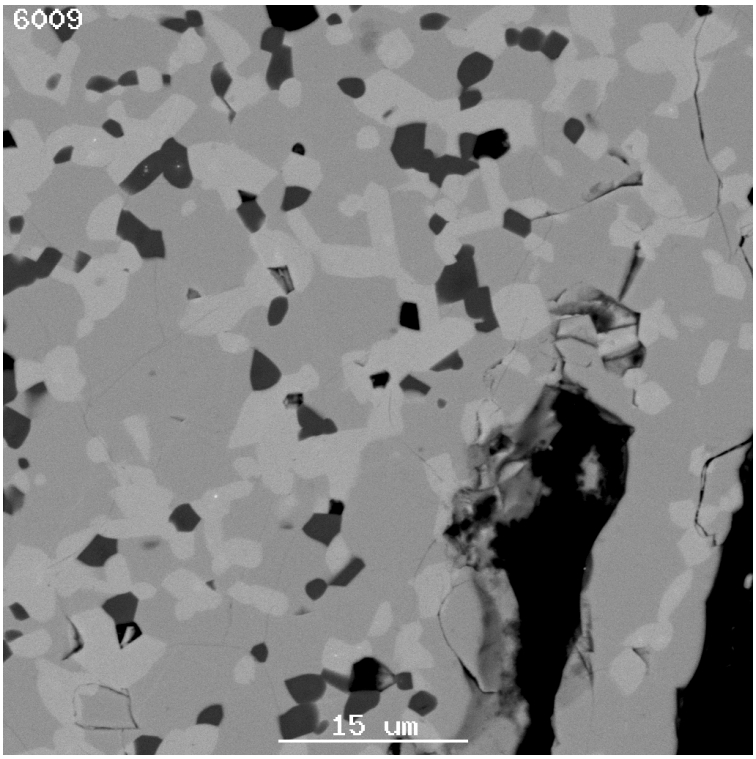


Figure A-4: (a), (b) and (c) backscatter electron micrographs of mws99-0606 (composition B1-2, oxide-route, wet-attrition milled, sintered at 1350°C in Ar for 4 hours). Micrograph (b) shows the exterior of the pellet and (c) the interior of the pellet. The matrix is pyrochlore. Th/U-brannerite (grey grains), Hf-doped rutile (dark-grey) ThO_2 (white spots in brannerite grains) and porosity (black) is also present.

(b)



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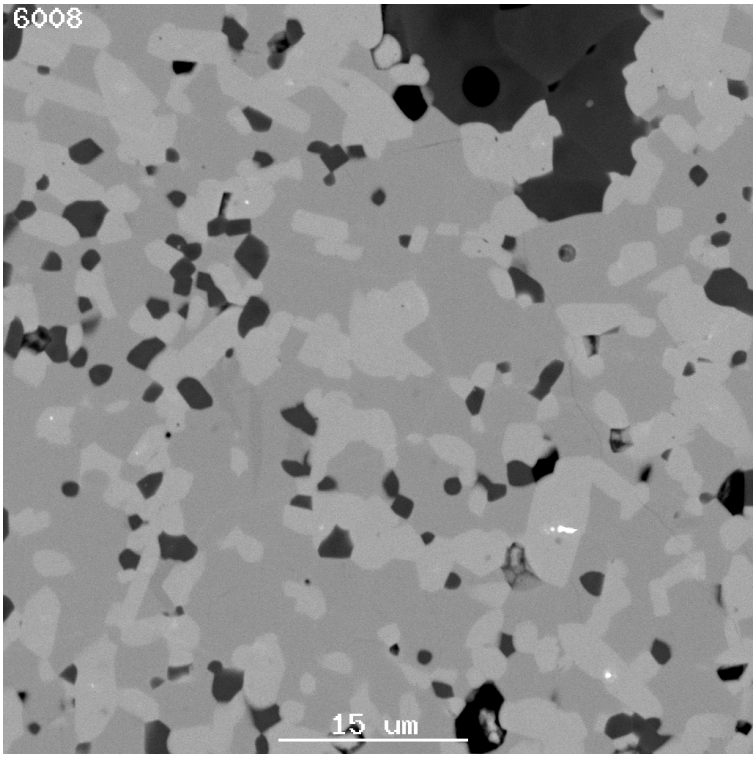


A.2 EDS ANALYSES

Table A-1: EDS analyses of phases (number of cations) in the pellet of composition B1-2, Th/U-doped oxide-route batch, which was we milled 16 hours and sintered in Ar at 1350°C for 4 hours.

Sample No.	**mws980137**				
	pyrochlore	**4M zirconolite**	**brannerite**	**rutile**	**Th/U Oxide**
~ abundance (vol. %)	65 - 70	5	20 - 25	3	1
Element					
oxygen	7	7	6	2	2
Ca	1.03	0.99	0.09	0.009	0.005
Gd	0.24	0.22	0.14		
Hf	0.25	0.42	0.13	0.07	
Th	0.15	0.09	0.31	0.001	0.87
U $^{\$}$	0.41	0.31	0.43	0.005	0.09
Ti	1.99	2.02	1.99	0.92	0.04
Total	4.08	4.05	3.08	1.01	1.00

$ The uranium is taken to be U^{4+} for analysis purposes.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system. The standard error in the individual measurements is ~ 1 %.

Table A-2: EDS analyses of phases (number of cations) of the pellet mws990441 (B1-2, baseline composition, oxide-route wet ball mille for 16 hours) that had been sintered in air at 1350°C for 4 hours. The exterior EDS measurements were taken within the outer 20 μm o the pellet and the interior EDS measurements were taken > 100μm from the outside of the pellet.

	interior			exterior		
Phase	**pyrochlore**	**brannerite**	**rutile**	**pyrochlore**	**brannerite**	**rutile**
~ abundance (vol. %)	65-75	20-30	5	68-80	20-30	0 - 2
Element						
oxygen	7	6	2	7	6	2
Ca	1.08	0.08	0.005	1.09	0.10	0.003
Gd	0.21	0.13	0.003	0.22	0.15	0.001
Hf	0.25	0.15	0.10	0.26	0.15	0.09
Th	0.15	0.34	0.001	0.13	0.31	0.001
U [$]	0.46	0.37	0.006	0.45	0.38	0.005
Ti	1.94	2.01	0.89	1.95	2.00	0.90
Total	4.10	3.08	1.00	4.10	3.09	1.00

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the individual measurements is ~ 1 %.

Table A-3: EDS analyses of phases (number of cations) of the pellet mws99-0527 (B1-2, baseline composition, oxide-route dry ball milled) that had been sintered in air at 1350°C for 4 hours. The exterior EDS measurements were taken within the outer 20 μm of the pellet and the interior EDS measurements were taken > 100μm from the outside of the pellet.

	interior			exterior		
Phase	**pyrochlore**	**brannerite**	**rutile**	**pyrochlore**	**brannerite**	**rutile**
~ abundance (vol. %)	65-75	20-30	5-7	69-77	20-30	1 - 3
Element						
oxygen	7	6	2	7	6	2
Ca	1.07	0.09	0.005	1.06	0.08	0.001
Gd	0.23	0.12	0.004	0.23	0.13	
Hf	0.24	0.14	0.08	0.24	0.14	0.08
Th	0.15	0.35	0.005	0.16	0.36	0.001
U [$]	0.43	0.36	0.009	0.44	0.36	0.005
Ti	1.96	2.02	0.90	1.96	2.00	0.91
Total	4.10	3.08	1.00	4.09	3.07	1.00

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the individual measurements is ~ 1 %.

Table A-4: EDS analyses of phases (number of cations) of the pellet mws99-0606 (B1-2, baseline composition, oxide-route wet attrition milled) that had been sintered in air at 1350°C for 4 hours. The exterior EDS measurements were taken within the outer 20 μm of the pellet and the interior EDS measurements were taken > 100μm from the outside of the pellet.

	interior			exterior		
Phase	**pyrochlore**	**brannerite**	**rutile**	**pyrochlore**	**brannerite**	**rutile**
~ abundance (vol. %)	65-75	15-25	5-7	72 - 86	15-25	1 - 3
Element						
oxygen	7	6	2	7	6	2
Ca	1.04	0.06	0.002	1.05	0.07 – 0.13	0.004
Gd	0.29	0.15 – 0.18	0.001	0.25	0.13-0.17	0.001
Hf	0.27	0.07 – 0.14	0.08	0.27	0.15	0.09
Th	0.15	0.33 – 0.37	0.001	0.15	0.32-0.34	0.001
U [$]	0.41	0.35	0.003	0.41	0.36	0.005
Ti	1.94	2.02	0.91	1.96	1.99	0.90
Total	4.10	3.08 [#]	1.00	4.09	3.07 [#]	1.00

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
# The total was constant even though the composition varied.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system. The standard error in the individual measurements is ~ 1 %.

A.3 XRD RESULTS

Table A-5: A summary of the XRD results for B1-2 (Th/U/Hf-baseline ceramic) samples.

Description - Processing Route			
Route/Milling/Sint. Temp. (^{o}C)/ Sint. atmosphere/Sample No.	**XRD Description**	**XRD File Name.**	**Phases Present**
oxide/wet ball/1350/Ar/ mws990434	As fired pellet top surface	t1494	pyrochlore, brannerite, possibly rutile
	As fired pellet bottom surface	t1500	pyrochlore, brannerite, possibly rutile
	Powder with W reference.	t1617	pyrochlore, brannerite, possibly rutile, tungsten
oxide/wet ball/1350/air/ mws990441	As fired pellet top surface	t1517	pyrochlore, brannerite, rutile
	As fired pellet bottom surface	t1593	pyrochlore, brannerite, possibly rutile
	Ground surface of pellet	t1805	pyrochlore, brannerite, rutile
	Powder with W reference.	t1860	pyrochlore, brannerite, rutile, tungsten
oxide/dry ball/1350/air/ mws99-0527	Ground surface of pellet	s15952	pyrochlore, brannerite, rutile
oxide/wet attrition/1350/air/ mws00-0606	As fired pellet top surface	s16207	pyrochlore, brannerite, possibly rutile
	ground surface of pellet	s16198	pyrochlore, brannerite, possibly rutile
	Powder with W reference	t2560	pyrochlore, brannerite, tungsten

The above Table contains a list of the raw XRD data files. Note that those starting with t are Scintag Diffractometer files (Cu K-alpha radiation) and those starting with S are Siemens D500 Diffractometer data files (Co K-alpha). The broad low angle peak ~ 15 - 25° (2 theta) in some of the patterns is from the resin used to mount the samples. The raw data files are given on the enclosed computer disk.

s*.raw files are Siemens D500 files.

t*.raw files are Scintag raw files using DMSNT Version 1.3 (Diffraction Management System) for Microsoft Windows NT 4.0, t*.txt are text files of Scintag files, t*.rd are Scintag files exported as older version Scintag binary files.

A.3.1 Oxide-route Wet Ball Milled Sample Fired at 1350^{o}C in Ar

The XRD patterns of the top and bottom of the pellet are different with possibly some minor preferred orientation of the pyrochlore in the bottom of the pellet. The pattern from powdered sample is similar to that from the top of the pellet.

A.3.2 Oxide-route Wet Ball Milled Sample Fired at 1350^{o}C in Air

The XRD patterns of top, bottom and ground surfaces and powder of the pellet are similar. The patterns are similar to those for the Ar sintered sample except for slightly more intense brannerite peaks.

A.3.3 Oxide-route Dry Ball Milled Sample Fired at 1350^{o}C in Air

The XRD pattern of the ground surface has more intense brannerite peaks than the XRD patterns of the equivalent wet milled samples.

A.3.4 Oxide-route Attrition Milled Sample Fired at 1350^{o}C in Air

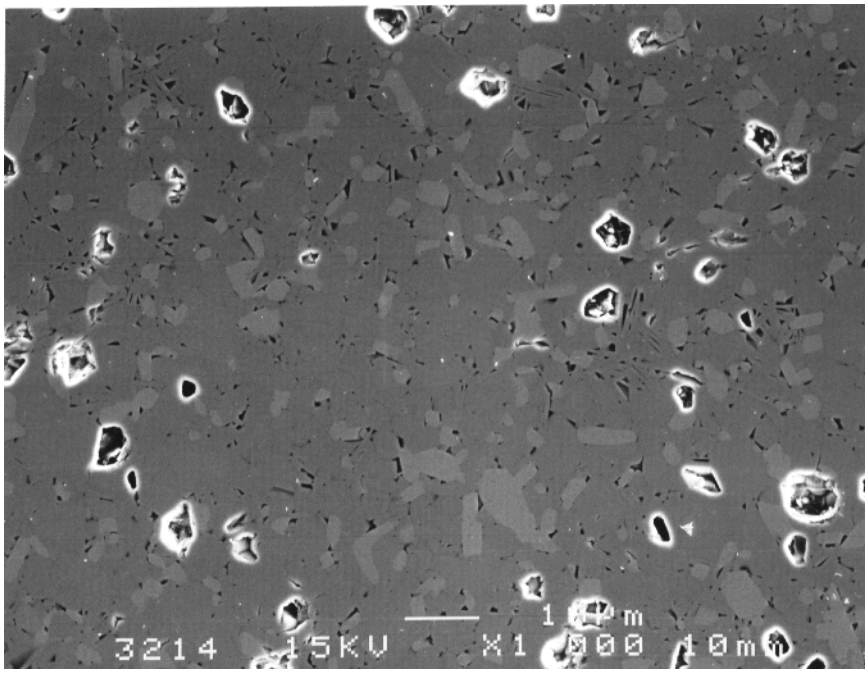
The brannerite peaks are more intense in the ground surface XRD pattern than in the exterior top surface pattern. The pattern from the powdered sample is also similar to that from the ground surface.

APPENDIX B

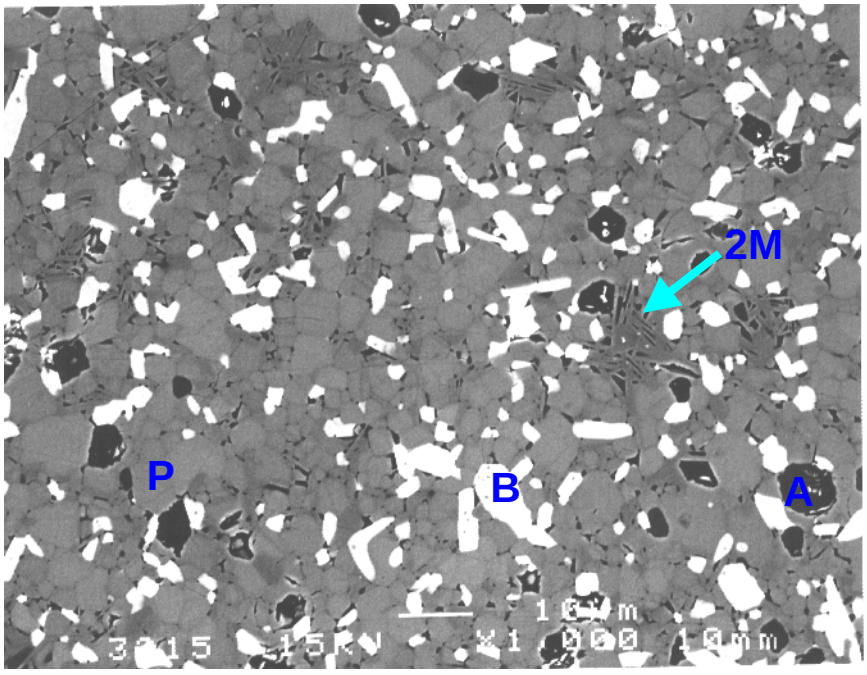
SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-4 - Th/U-DOPED BASELINE + IMPURITIES CERAMIC

B. APPENDIX B: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-4 - TH/U-DOPED BASELINE + IMPURITIES CERAMIC

B.1 SEM IMAGES

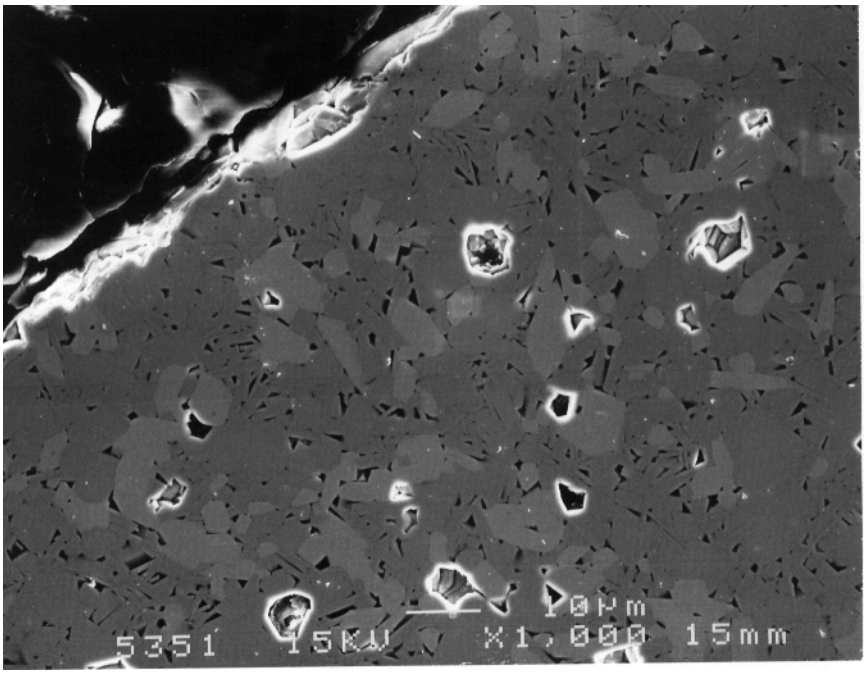


(a)

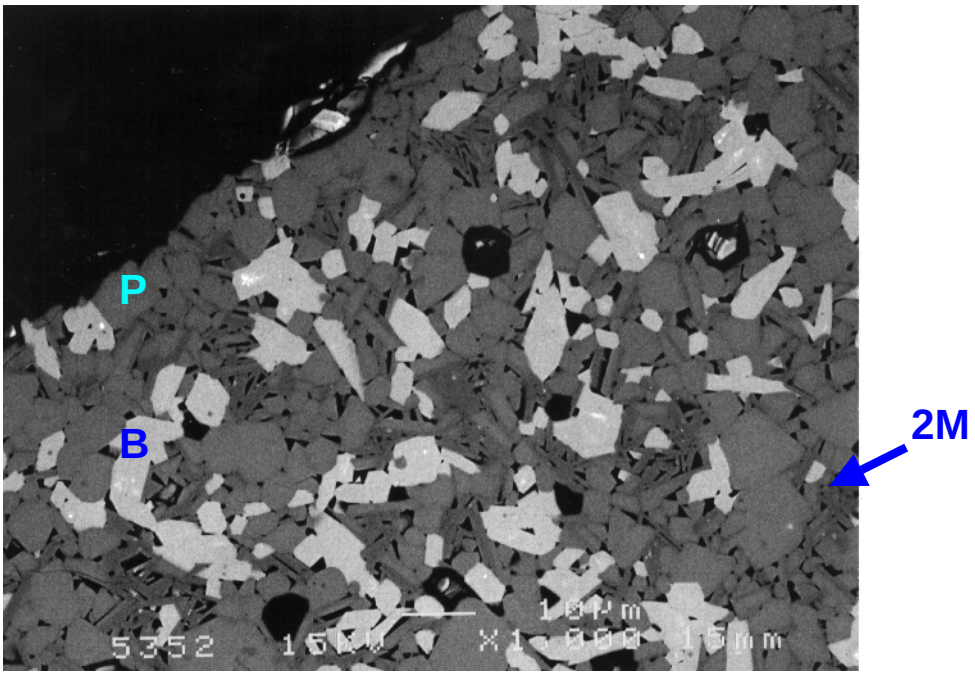


(b) 10 µm.

Figure B-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980149 (Task 1.2, composition B1-4, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore (P), the light-grey phase is Th/U-brannerite (B) and the elongated grains are 2M zirconolite (2M). Porosity (A) is also present. An intergranular silicate phase is present at triple points. The rounded grains are indicative of liquid phase sintering.



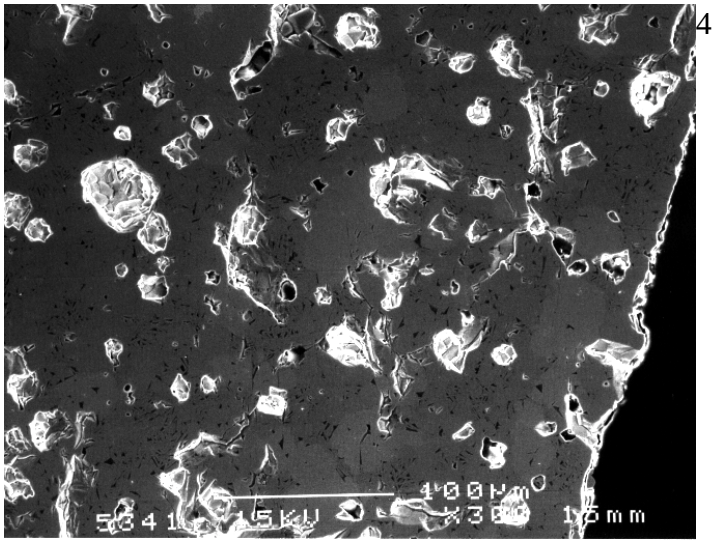
(a)



(b) 10 µm.

Figure B-2: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws990442 (Task 1.2, composition B1-4, oxide-route, wet-milled 16 hours, sintered at 1350°C in air for 4 hours). The matrix is pyrochlore (P), the elongated grains are 2M zirconolite (2M), the light-grey phase is Th/U-brannerite (B), and some $(Th,U)O_2$ (white spots) is also present inside some of the brannerite grains. Porosity (see (a)) is also present. An intergranular silicate phase is present at triple points.

(a)



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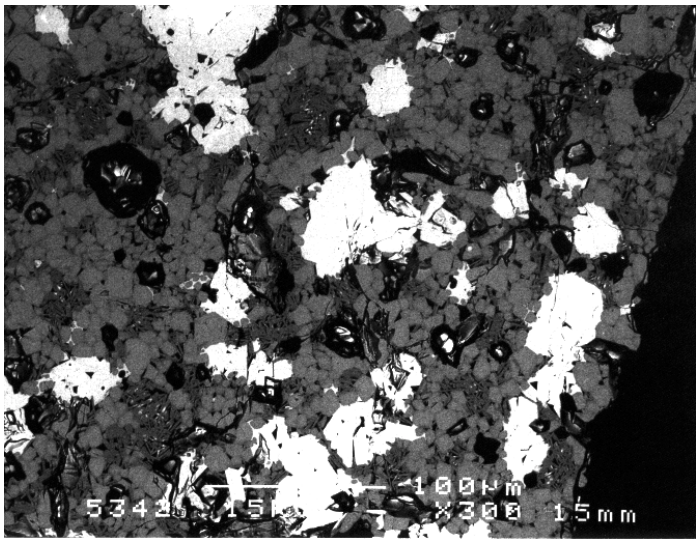


(c)

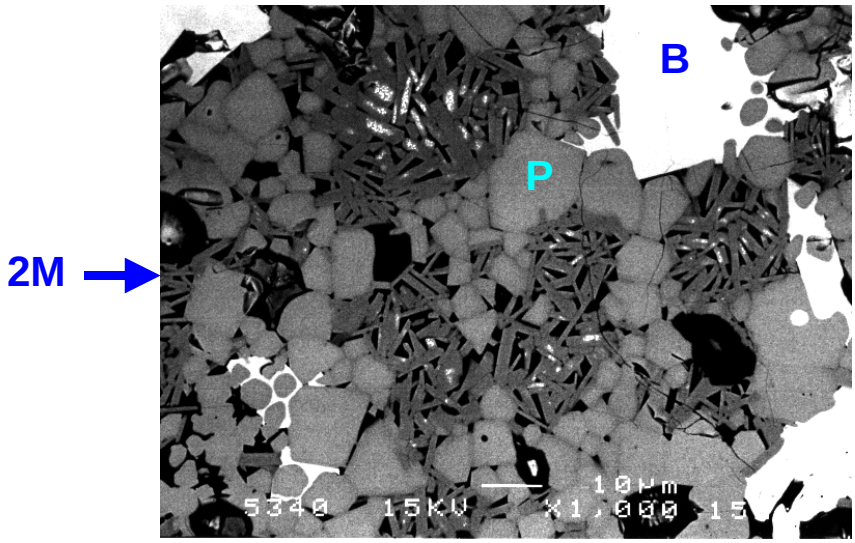


Figure B-3: (a) Secondary electron micrograph and (b) and (c) backscattered electron micrographs of mws99-0528 (Task 1.2, composition B1-4, oxide-route, dry-milled 16 hours, sintered at 1350°C in air for 4 hours). Micrograph (c) is of the interior of the sample; the exterior is similar (see (b). The matrix is pyrochlore (P), the elongated grains are 2M zirconolite (2M), the light-grey phase is Th/U-brannerite (B), and some $(Th,U)O_2$ (white spots) is also present inside some of the brannerite grains. Some hafnium oxide (white regions, see (c)) was detected inside some zirconolite grains. An intergranular silicate

(a)

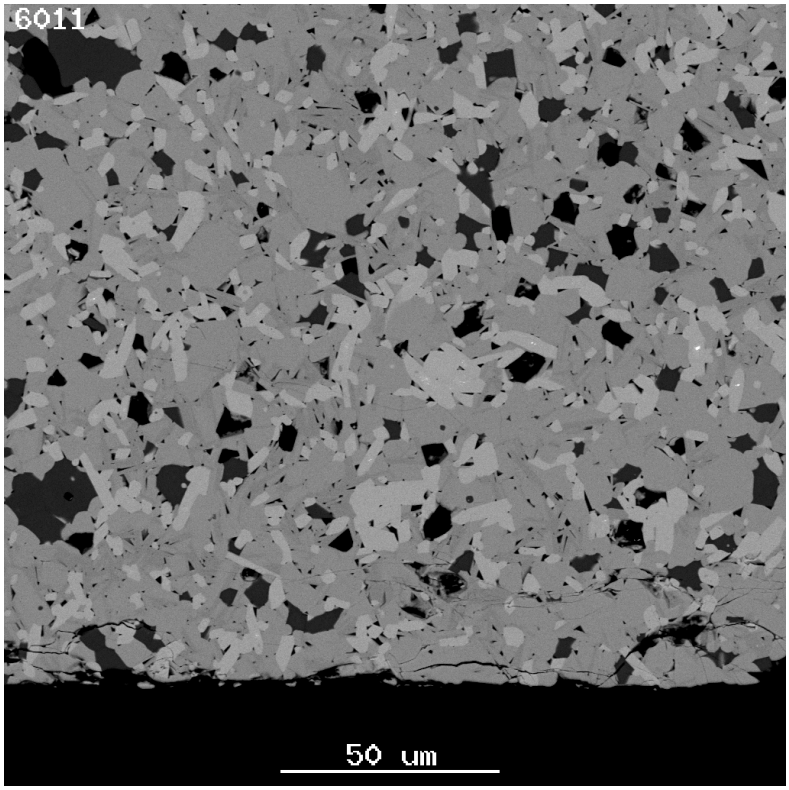
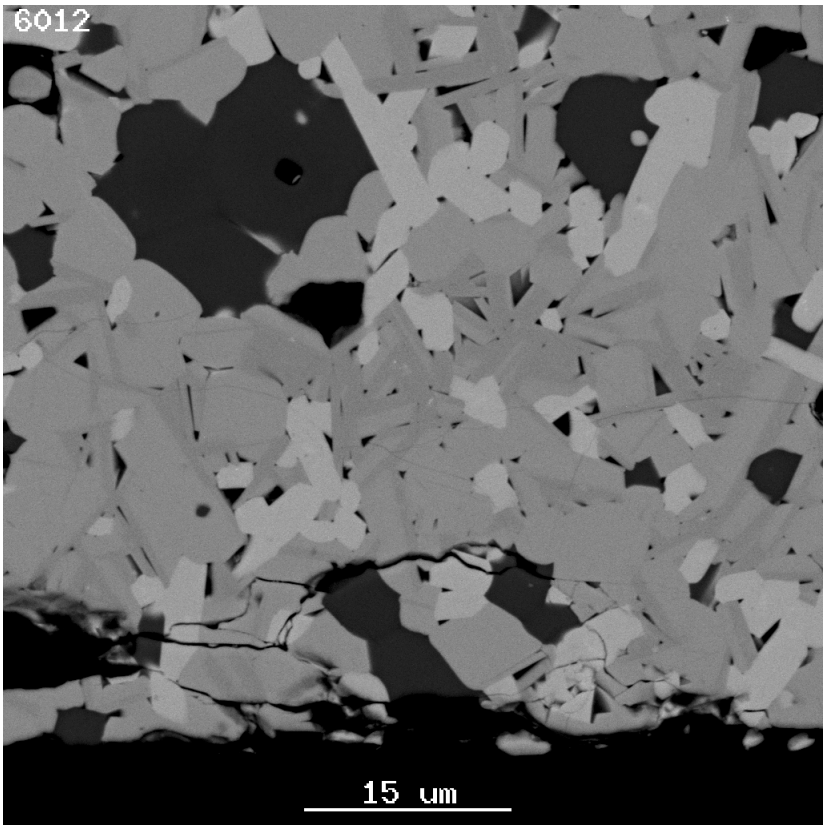


Figure B-4: (a), (b) and (c) backscattered electron micrographs of mws99-0608 (composition B1-4, oxide-route + impurities, wet-attrition milled, sintered at 1350°C in air for 4 hours). Micrograph (b) shows the exterior of the pellet and (c) the interior of pellet. The matrix is pyrochlore with 2M zirconolite, the slightly darker elongated grains in (b) and (c). Th/U-brannerite (light grey grains), Hf-doped rutile (dark-grey), ThO_2 (white spots in brannerite grains) and porosity (black) are also present.

(b)



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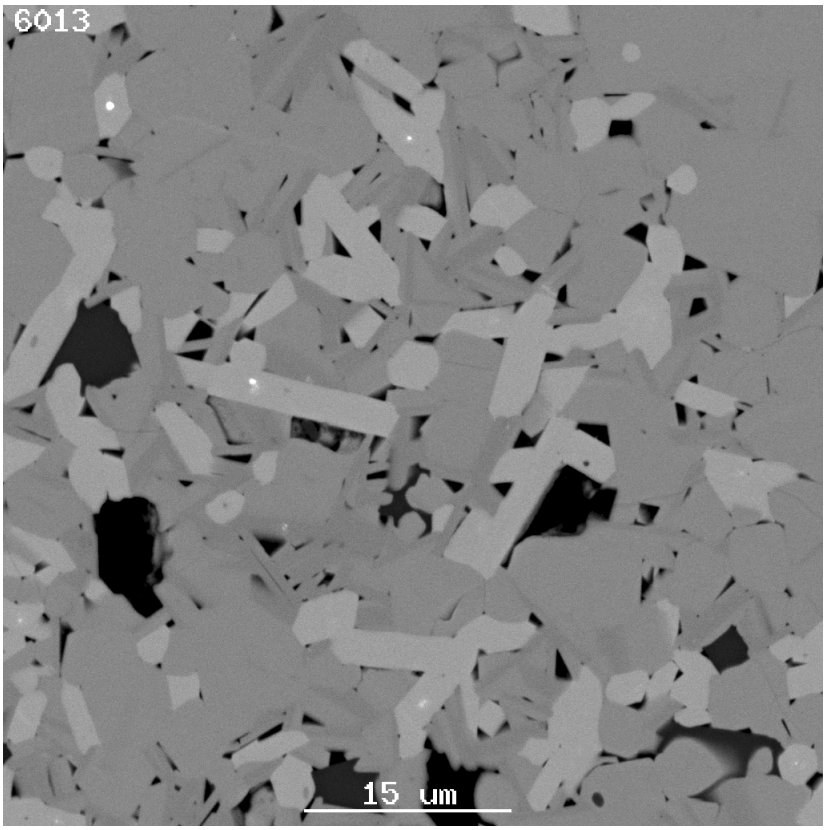


B.2 EDS ANALYSES

Table B-1: EDS analyses of phases (number of cations, except for the silicate phase, which is given in wt. % of element) in the sample of composition B1-4, Th/U-doped oxide-route batch, which was wet-milled for 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.

Sample No.	**mws980149**			
	pyrochlore	**2M zirconolite**	**brannerite**	**Silicate Phase** *
~ abundance (vol. %)	78 - 79	10	10	1 - 2
Element				**Wt. %**
oxygen	7	7	6	41
Ca	0.99	0.75	0.03	14
Gd	0.26	0.20	0.08	1.6
Hf	0.17	0.65	0.06	1
U $	0.44	0.17	0.24	2
Th	0.18	0.06	0.67	1
Ti	1.95	1.85	1.93	6
Mg	0.05	0.06		2
Al	0.02	0.14	0.03	7
Ga		0.14		5.5
K				
Na				
Si				14
Ta	0.02			
W	0.01			
Mo				0.7
Fe				0.2
P				3.5
B #				
Cr				
Zn				
Total	4.07	4.02	3.04	100

* Typical values – may have some interference from other phases due to small grain size.

$ The uranium is taken to be U^{4+} for analysis purposes.

B is not detected by the EDS system.

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system.

The standard error in the individual measurements is ~ 1 %.

Table B-2 - EDS analyses of phases (number of cations, except for the glass phase which is given in wt. % of element present) in sample mws990442 (B1-4, baseline + impurities composition, wet ball milled for 16 hours) that had been sintered in air at 1350°C for 4 hours. The exterior EDS measurements were taken within the outer 20 μm of the pellet and the interior EDS measurements were taken > 100μm from the outside of the pellet.

	interior					exterior				
Phase	**pyrochlore**	**brannerite**	**zirconolite**	**rutile [&]**	**Silicate Phase [*]**	**pyrochlore**	**brannerite**	**zirconolite**	**rutile [&]**	**Silicate Phase [*]**
~ abundance (vol. %)	70-80	10-15	10-15	< 1	1 - 2	70-80	10-15	10-15	< 1	1 - 2
Element					**(Wt. %)**					**(Wt. %)**
oxygen	7	6	7	2	35	7	6	7	2	37
Ca	1.06	0.08	0.73		11	1.07	0.08	0.73		10.5
Gd	0.20	0.12	0.18		3.5	0.21	0.11	0.18		3
Hf	0.17	0.10	0.67		2	0.17	0.10	0.68		3
Th	0.17	0.39	0.06		4.5	0.17	0.40	0.06		4
U [$]	0.47	0.37	0.16		10.5	0.47	0.36	0.16		8
Ti	1.94	1.97	1.85		10	1.92	1.96	1.83		9
Al	0.03	0.04	0.11		4	0.03	0.06	0.11		4.5
Mg	0.02		0.10		1.5	0.03		0.10		2
Ga			0.18		3			0.20		4
Ta	0.02					0.03				
W	0.008					0.005				
Mo										
Na					1					1
K					0.5					0.5
Si					10					11
B [#]										
Fe					0.1					0.2
Cr										
Ni										
P					3					3
Total	4.10	3.08	4.03		100	4.10	3.08	4.04		100

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

B is not detected by the EDS system.

& Rutile is present as a few small grains < 1 μm, but was not analysed.

* The glass composition is variable across the sample and the analysis is prone to error, values here are given as a guide only.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

The standard error in the individual measurements is ~ 1 %.

Table B-3 - EDS analyses of phases (number of cations, except for the glass phase which is given in wt. % of element present) in the sample mws99-0528 (B1-4, baseline impurities composition, dry ball milled for 16 hours) that had been sintered in air at 1350°C for 4 hours. The exterior EDS measurements were taken within the outer 2(μm of the pellet and the interior EDS measurements were taken > 100μm from the outside of the pellet. Hafnia is included, but was t0o small a grain size to analyse.

	interior						exterior					
Phase	**pyrochlore**	**brannerite**	**zirconolite**	**rutile [&]**	**Hafnia**	**Silicate Phase [*]**	**pyrochlore**	**brannerite**	**zirconolite**	**rutile [&]**	**Hafnia**	**Silicate P**
~ abundance (vol. %)	55-60	25	15	<1	<1	1-2	55-60	25	15	<1	<1	1-2
Element						**(Wt. %)**						**(Wt.**
oxygen	7	6	7	2	2	38	7	6	7	2	2	39
Ca	1.05	0.08	0.72	0.003		13	1.04	0.07	0.74	0.004		12
Gd	0.21	0.13	0.15	0.001		2	0.22	0.09 - 0.13	0.17	0.002		1.5
Hf	0.18	0.12	0.74	0.04		4.5	0.18	0.11	0.73	0.04		5
Th	0.16	0.39	0.05	0.001		1.5	0.16	0.34 – 0.45	0.05	0.006		1
U [$]	0.46	0.38	0.15	0.01		5	0.46	0.34 – 0.39	0.15	0.01		2
Ti	1.93	1.93	1.79	0.94		8.5	1.94	1.95	1.79	0.93		7
Al	0.04	0.07	0.20	0.01		4.5	0.05	0.06	0.18	0.01		6
Mg	0.03		0.08			1	0.03		0.09			2
Ga			0.14			5			0.15			5.5
Ta	0.02			0.004			0.02			0.004		
W	0.01						0.01					
Mo												
Na						0.5						1
K						0.5						0.5
Si						11						12.
B [#]												
Fe						0.1						0.2
Cr												
Ni												
P						3						3
Total	4.10	3.09	4.02	1.00		100	4.09	3.08 [+]	4.05	1.00		10(

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

& Rutile is present as small grains < 1 μm, but was not analysed.

B is not detected by the EDS system.

+ Despite compositional variations the elements always added up to this total.

* The glass composition is variable across the sample and the analysis is prone to error, values here are given as a guide only.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

The standard error in the individual measurements is ~ 1 %.

Table B-4 - EDS analyses of phases (number of cations, except for the glass phase which is given in wt. % of element present) in the samplemws99-0608 (B1-4, baseline + impurities composition, wet attrition milled) that had been sintered in air at 1350°C for 4 hours. The exterior EDS measurements were taken within the oute 20 μm of the pellet and the interior EDS measurements were taken > 100μm from the outside of the pellet.

	interior					exterior				
Phase	**pyrochlore**	**brannerite**	**zirconolite**	**rutile [&]**	**glass [*,+]**	**pyrochlore**	**brannerite**	**zirconolite**	**rutile [&]**	**glass [*]**
60-70	15-20	10-15	5	1-2	1-2	60-70	15-20	10-15	5	1-2
Element					**(Wt. %)**					**(Wt. %)**
oxygen	7	6	7	2		7	6	7	2	35
Ca	1.03	0.09	0.75	0.005		1.01	0.07	0.77	0.001	13
Gd	0.24	0.13	0.19	0.001		0.24	0.13	0.20		4
Hf	0.16	0.12	0.65	0.06		0.17	0.12	0.64	0.06	7
Th	0.17	0.36	0.06	0.001		0.17	0.36	0.06	0.001	2.5
U [$]	0.42	0.36	0.14	0.01		0.42	0.38	0.13	0.01	8
Ti	1.96	1.97	1.90	0.91		1.96	1.97	1.89	0.91	9
Al	0.03	0.04	0.11	0.01		0.05	0.05	0.11	0.015	4
Mg	0.02		0.09			0.02		0.10		1.5
Ga	0.02	0.01	0.15					0.16		2.5
Ta	0.02	0.01		0.01		0.02	0.01		0.005	
W	0.01					0.01				
Mo										
Na										1
K										0.1
Si										10
B [#]										
Fe										0.1
Cr										
Ni										
P										3
Total	4.08	3.09	4.04	1.01	100	4.08	3.08	4.04	1.00	100

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

& Rutile is present as small grains < 1 μm, but was not analysed.

* The glass composition is variable across the sample and the analysis is prone to error, values here are given as a guide only.

\# B is not detected by the EDS system.

\+ Composition analysed, but too much interference from surrounding grains.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system. The standard error in the individual measurements is ~ 1 %..

B.3 XRD RESULTS

Table B-5: A summary of the XRD results for samples made of composition B1-4 (Th/U/Hf-baseline + impurities ceramic).

Description - Processing Route			
Route/Milling/Sint. Temp. (°C)/ Sint. atmosphere/Sample No.	**XRD Description**	**XRD File Name.**	**Phases Present**
oxide/wet ball/1350/Ar/ mws990435	As fired pellet top surface	t1495	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at 0.557 nm
	As fired pellet bottom surface	t1501	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at 0.557 nm
	Powder with W reference.	t1768	pyrochlore, brannerite, 2M zirconolite, tungsten
oxide/wet ball/1350/air/ mws990442	As fired pellet top surface	t1553	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at 0.557 nm
	As fired pellet bottom surface	t1594	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at 0.557 nm
	Ground surface of pellet	t1740	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at 0.557 nm
	Powder with W reference.	t1861	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at 0.557 nm, tungsten
oxide/dry ball/1350/air/ mws00-0528	ground surface of pellet	s15953	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at 0.557 nm
oxide/wet attrition/1350/air/ mws00-0608	As fired pellet top surface	s16200	pyrochlore, brannerite, rutile, 2M zirconolite + additional "zirconolite" peak at 0.557 nm
	Ground surface of pellet	s16209	pyrochlore, brannerite, rutile, 2M zirconolite + additional "zirconolite" peak at 0.557 nm
	Powder with W reference	t2561	pyrochlore, brannerite. 2M zirconolite + additional "zirconolite" peak at 0.557 nm, tungsten

The above Table contains a list of the raw XRD data files. Note that those starting with t are Scintag Diffractometer files (Cu K-alpha radiation) and those starting with S are Siemens D500 Diffractometer data files (Co K-alpha). The broad low angle peak ~ 15 - 25° (2 theta) in some of the patterns is from the resin used to mount the samples. The raw data files are on the enclosed computer disk.

s*.raw files are Siemens D500 files.

t*.raw files are Scintag raw files using DMSNT Version 1.3 (Diffraction Management System) for Microsoft Windows NT 4.0, t*.txt are text files of Scintag files, t*.rd are Scintag files exported as older version Scintag binary files.

B.3.1 Oxide-route Wet Ball Milled Sample Fired at 1350^{o}C in Ar

The XRD patterns of the top and bottom of the pellet are similar except for possibly some minor differences in the preferred orientation of the zirconolite. An additional peak at ~ 0.557 nm was observed. The XRD pattern of the powdered sample is different to that of the solid surfaces. The 0.557 nm peak is barely detectable, the zirconolite peaks are much less intense and the brannerite peaks are more intense. We intend to repeat this work to check these results.

B.3.2 Oxide-route Wet Ball Milled Sample Fired at 1350^{o}C in Air

The XRD patterns of the top and bottom of the pellet are different. There appears to be slightly more intense zirconolite peaks in the pattern of the bottom surface. The additional peak at ~ 0.557 nm was also observed in the XRD patterns of both the top and bottom of the pellets. The ground surface pattern has less intense zirconolite peaks and a prominent but smaller 0.557 nm peak. The XRD pattern of the powdered sample is similar to that of the ground pellet except that the 0.557 nm peak is much smaller, the zirconolite peaks are much less intense and the brannerite peaks are more intense.

B.3.3 Oxide-route Dry Ball Milled Sample Fired at 1350^{o}C in Air

The XRD pattern of the ground surface is similar to that of the equivalent wet ball milled sample. The 0.557 nm peak is present.

B.3.4 Oxide-route Attrition Milled Sample Fired at 1350^{o}C in Air

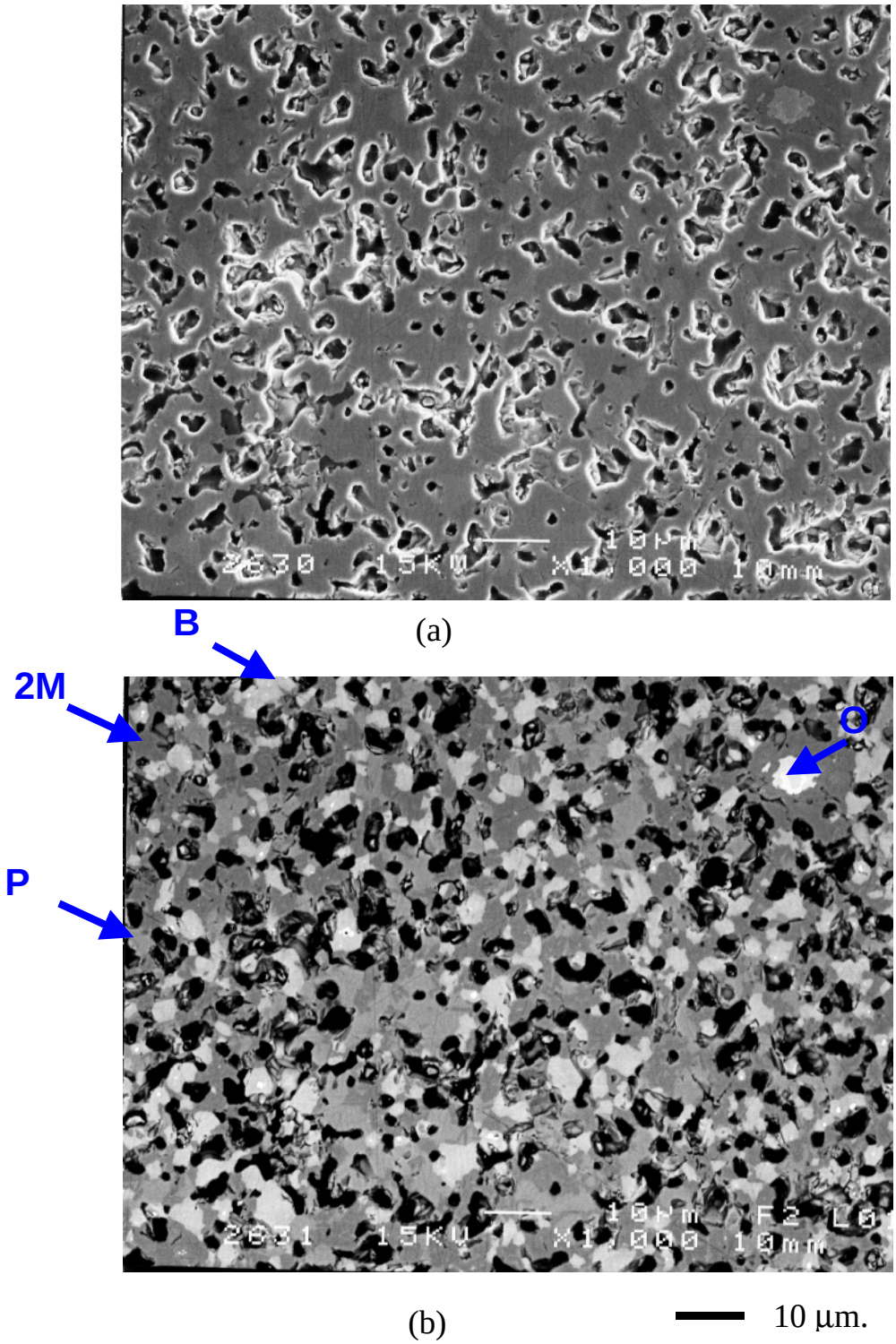
The results are very similar to those of the wet ball milled sample sintered in air (see B.3.2 above).

APPENDIX C

SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-10 - Th/U-DOPED ZIRCONOLITE-RICH CERAMIC

C. APPENDIX C: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-10 - TH/U-DOPED ZIRCONOLITE-RICH CERAMIC

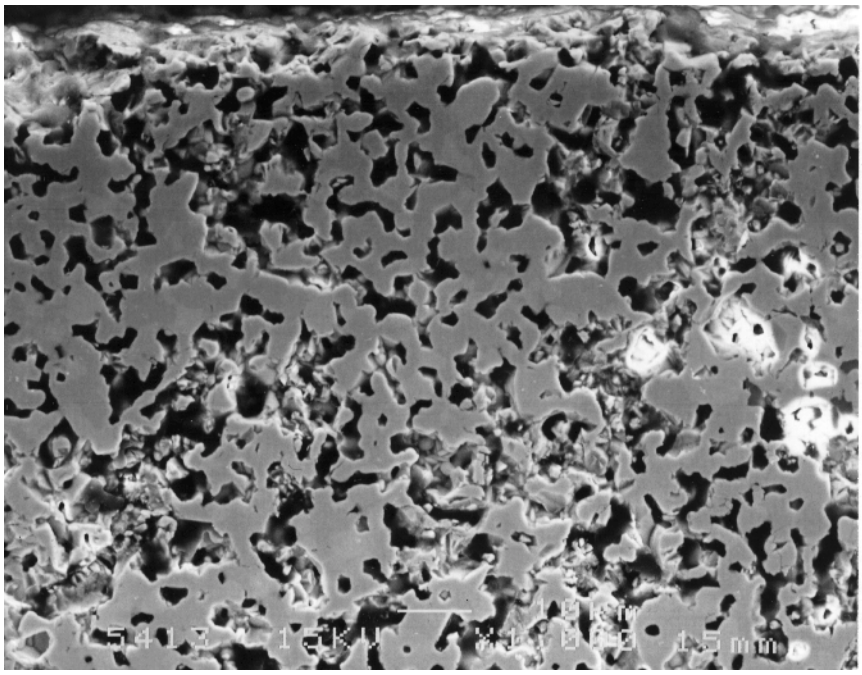
C.1 SEM IMAGES



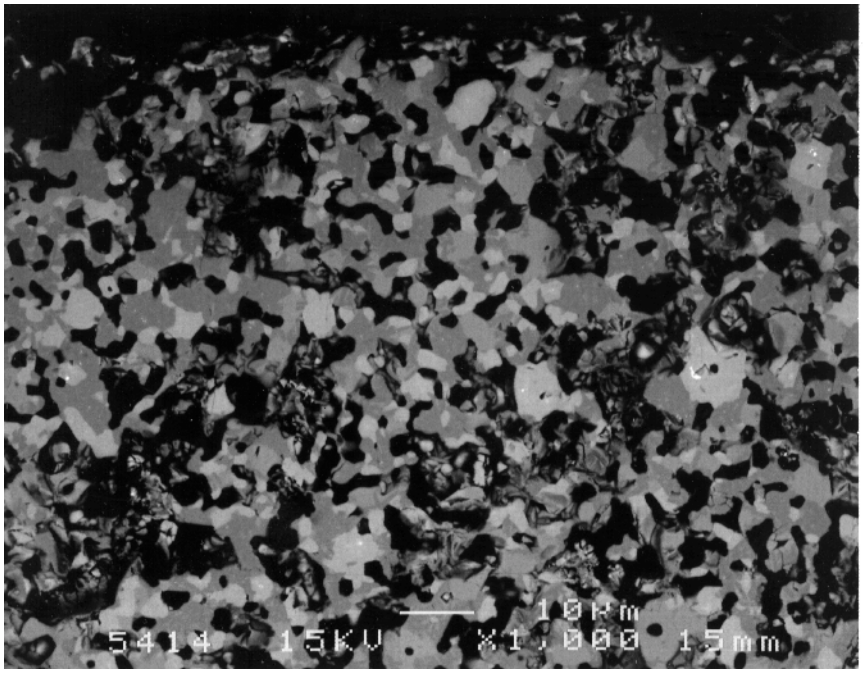
(a)

(b)

Figure C-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980145 (composition B1-10, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The sample consists mainly of pyrochlore (mid-grey), 2M zirconolite (2M, darker grey) and Th/U-brannerite (B, light-grey). Some (< 1 vol. %) grains of ThO_2-UO_2 (O) are also present inside the brannerite grains. The sample is very porous (see (a))



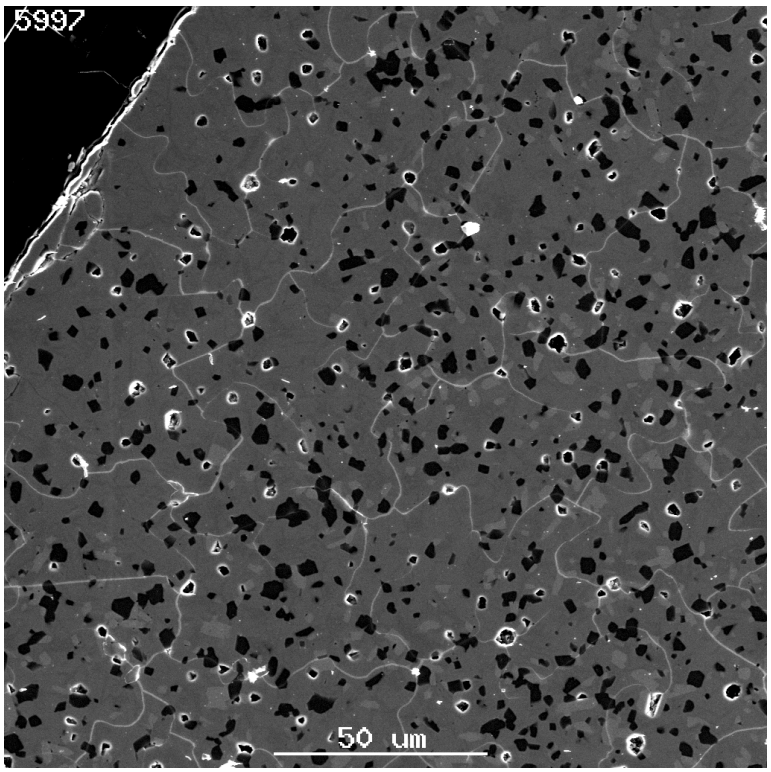
(a)



(b) 10 µm.

Figure C-2: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws990443 (composition B1-10, oxide-route, wet-milled 16 hours, sintered at 1350°C in air for 4 hours). The sample is very porous. It consists mainly of pyrochlore (mid-grey), 2M zirconolite (darker grey) and Th/U-brannerite (light-grey). Some (< 1 vol. %) ThO_2-UO_2 is also present inside brannerite grains (white spots).

(a)



(b)

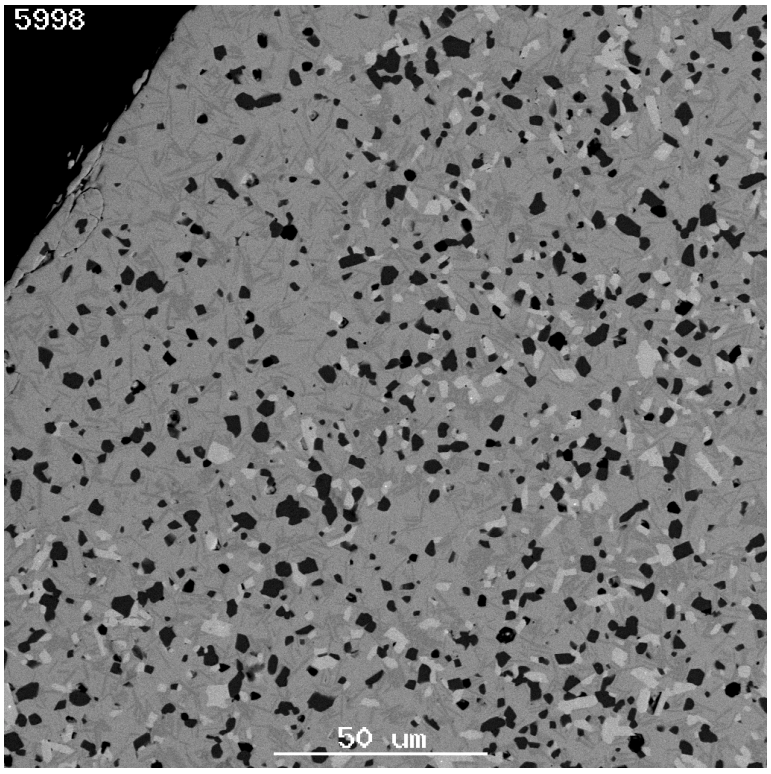
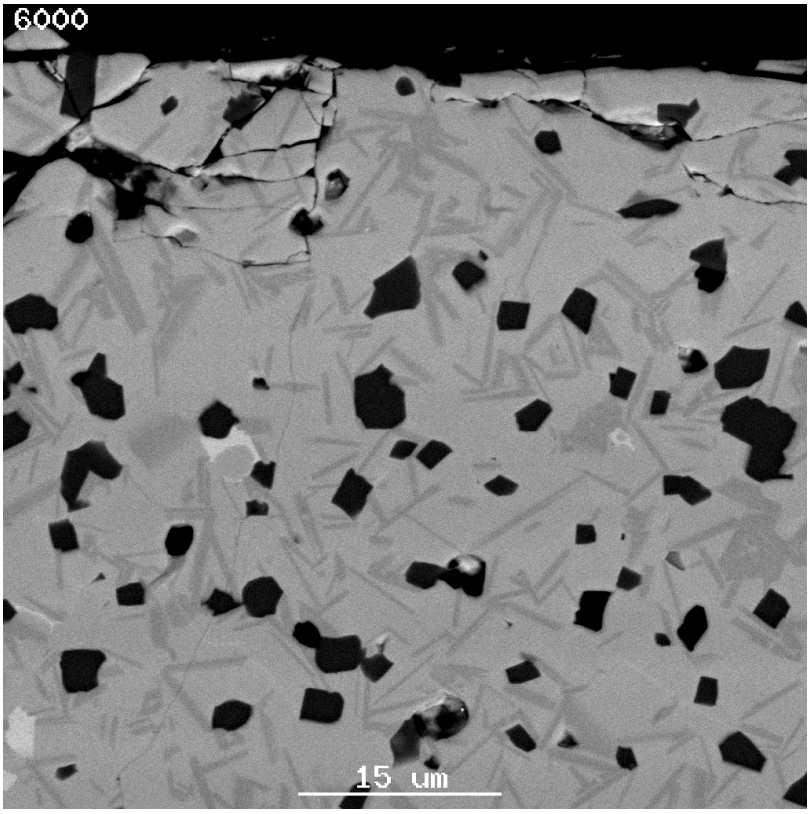
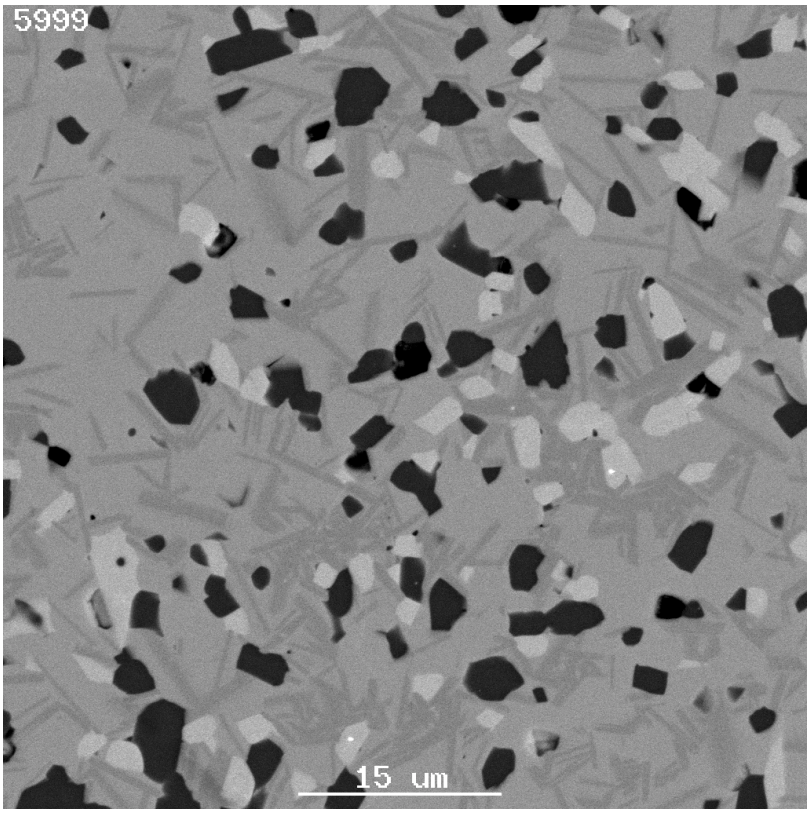


Figure C-3: (a) Secondary electron micrograph and, (b), (c) and (d) backscatter electron micrographs of mws99-0602 (composition B1-10, oxide-route, attrition milled, sintered at 1350°C in air for 4 hours). Micrograph (c) shows the exterior of the pellet and (d) the interior of pellet. The sample consists of a matrix of pyrochlore (mid-grey) and 2M zirconolite (darker grey). Th/U-brannerite (light-grey) with some (~ 1 vol. %) ThO_2-UO_2 (white spots) inside some brannerite grains is also present; as is rutile (dark-grey) and porosity. The white lines in (a) are from a defect in

(c)



(d)



C.2 EDS ANALYSES

Table C-1: EDS analyses of phases (number of cations) in the pellet made from composition B1-10, Th/U-doped oxide-route batch, which was wet-milled ball milled for 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.

Sample No.	**mws980145**				
	pyrochlore	**2M zirconolite**	**brannerite**	**Oxide ThO_2 &**	**Oxide UO_2**
~ abundance (vol. %)	40 - 50	30 – 40	20	< 1	< 1
Element					
oxygen	7	7	6	2	2
Ca	0.99	0.83	0.03		0.04
Gd	0.29	0.17	0.07		0.03
Hf	0.26	0.75	0.13		0.01
U	0.40	0.10	0.41		0.87
Th	0.18	0.04	0.41		0.03
Ti	1.96	1.92	1.98		0.05
Al		0.20	0.02		
Total	4.07	4.01	3.04		1.03

& Too small to analyse accurately.

$ The uranium is taken to be U^{4+} for analysis purposes.

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

The standard error in the individual measurements is ~ 1 %.

Table C-2 - EDS analyses of phases (number of cations) found in the pellet mws990443 (B1-10, zirconolite-rich composition wet ball milled for 16 hours) that had been sintered in air at 1350°C for 4 hours. The exterior EDS measurements were taken within the outer 2 μm of the pellet and the interior EDS measurements were taken > 100μm from the outside of the pellet.

	interior					exterior				
Phase	**pyrochlore**	**zirconolite**	**brannerite**	**Th,U-oxide***	**rutile &**	**pyrochlore**	**zirconolite**	**brannerite**	**Th,U-oxide***	**rutile &**
~ Abundance (Vol. %)	40	40	20	<1	<1	40	40	20	<1	<1
Element										
oxygen	7	7	6		2	7	7	6		2
Ca	1.09	0.82	0.07			1.11	0.83	0.08		
Gd	0.19	0.13	0.10			0.20	0.13	0.08		
Hf	0.28	0.87	0.17			0.29	0.86	0.15		
Th	0.18	0.03	0.42			0.16	0.03	0.46-0.53		
U $	0.45	0.11	0.34			0.46	0.10	0.27-0.33		
Ti	1.86	1.80	1.91			1.87	1.81	1.92		
Al	0.06	0.24	0.07			0.03	0.24	0.05		
Total	4.11	4.01	3.08			4.11	4.01	3.08 +		

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

& Rutile is present but was not analysed; it contains Hf in a similar amount to previous samples (~ 0.07 - 0.1 formula units).

* Too small to analyse accurately.

\+ Despite compositional variations the elements always added up to this total.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the individual measurements is ~ 1 %.

Table C-3 - EDS analyses of phases (number of cations) found in the pellet mws99-0602 (B1-10, zirconolite-rich composition, attrition milled) that had been sintered in air at 1350°C for 4 hours. The exterior EDS measurements were taken within the outer 20 μm of the pellet and the interior EDS measurements were taken > 100μm from the outside of the pellet.

	interior					exterior				
Phase	**pyrochlore**	**zirconolite**	**brannerite**	**Th,U-oxide***	**rutile**	**pyrochlore**	**zirconolite**	**brannerite**	**Th,U-oxide***	**rutile &**
~ Abundance (Vol. %)	35-45	35-45	10-15	1	5-7	38-48	38-48	3	1	3
Element										
oxygen	7	7	6		2	7	6	7		2
Ca	1.03	0.78	0.06		0.001	0.99	0.81	0.07 – 0.10		0.003
Gd	0.24	0.18	0.10 – 0.13		0.001	0.23	0.17	0.10		0.001
Hf	0.14	0.60	0.08		0.04	0.14 - 0.18	0.50 – 0.56	0.10		0.04
Th	0.22	0.06	0.46		0.001	0.21 - 0.24	0.07 – 0.10	0.34 – 0.43		
U $	0.36	0.10	0.38		0.01	0.35 - 0.39	0.11 –0.16	0.26 – 0.33		0.01
Ti	2.03	1.96	1.97		0.94	2.01	1.96 - 1.99	1.95 – 2.13		0.94
Al	0.05	0.33	0.07		0.01	0.06	0.28 – 0.34	0.08		0.01
Total	4.09	4.01	3.08 +		1.00	4.08 +	4.03 +	3.09 +		1.01

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

* Too small to analyse accurately.

\+ Despite compositional variations the elements always added up to this total.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the individual measurements is ~ 1 %.

C.3 XRD RESULTS

Table C-4: A summary of the XRD results for samples made of composition B1-10 (Th/U/Hf-zirconolite-rich ceramic).

Description - Processing Route			
Route/Milling/Sint. Temp. (°C)/ Sint. atmosphere/Sample No.	**XRD Description**	**XRD File Name.**	**Phases Present**
oxide/wet ball/1350/Ar/ mws990436	As fired pellet surface top	t1496	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at ~ 0.56 nm
	As fired pellet surface bottom	t1502	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at ~ 0.56 nm
	Powder with W reference.	t1801	pyrochlore, brannerite, 2M zirconolite, tungsten
oxide/wet ball/1350/air/ mws990443	As fired pellet surface top	t1554	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at ~ 0.56 nm
	As fired pellet surface bottom	t1595	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at ~ 0.56 nm
	Ground surface of pellet	t1741	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at ~ 0.56 nm
	Powder with W reference.	t1862	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at ~ 0.56 nm, tungs
oxide/wet attrition/1350/air/ mws00-0602	As fired pellet surface top	s16194	pyrochlore, brannerite, rutile, 2M zirconolite + additional "zirconolite" peak at ~ 0.56 nm
	Ground surface of pellet	s16203	pyrochlore, brannerite, rutile, 2M zirconolite + additional "zirconolite" peak at ~ 0.56 nm
	Powder with W reference	t2558	pyrochlore, brannerite, 2M zirconolite + additional "zirconolite" peak at ~ 0.56 nm, tungs

The above Table contains a list of the raw XRD data files. Note that those starting with t are Scintag Diffractometer files (Cu K-alpha radiation) and those starting with S are Siemens D500 Diffractometer data files (Co K-alpha). The broad low angle peak ~ 15 - 25° (2 theta) in some of the patterns is from the resin used to mount the samples. The raw data files are on the enclosed computer disk.

s*.raw files are Siemens D500 files.

t*.raw files are Scintag raw files using DMSNT Version 1.3 (Diffraction Management System) for Microsoft Windows NT 4.0, t*.txt are text files of Scintag files, t*.rd are Scintag files exported as older version Scintag binary files.

C.3.1 Oxide-route Wet Ball Milled Sample Fired at 1350°C in Ar

The XRD patterns of the top and bottom of the pellet are similar. An additional peak at 0.557 nm was observed and this is slightly more intense in the pattern of the bottom of the pellet. The XRD pattern of the powdered sample is slightly different to that of the solid surfaces. The 0.557 nm peak is smaller, but detectable, and the zirconolite peaks are less intense.

C.3.2 Oxide-route Wet Ball Milled Sample Fired at 1350°C in Air

The XRD patterns of the top and bottom of the pellet are slightly different. The pattern of the bottom surface appears to have slightly more intense zirconolite peaks. The additional peak at ~ 0.557 nm was also observed in the XRD patterns of both the top and bottom of the pellets. The ground surface pattern is similar to that of the top of the pellet. The XRD pattern of the powdered sample is similar to that of the ground pellet.

C.3.3 Oxide-route Attrition Milled Sample Fired at 1350°C in Air

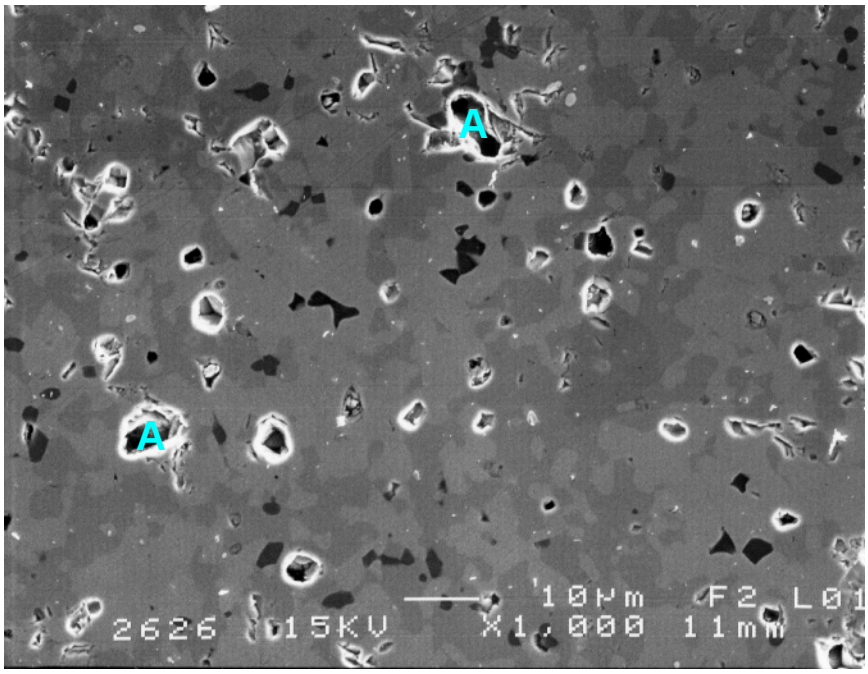
The results are very similar to those of the wet ball milled sample sintered in air (see preceding section) except that the brannerite peaks are less intense. The XRD pattern of the ground surface of the pellet has more intense brannerite and rutile peaks than the XRD pattern of the exterior surface.

APPENDIX D

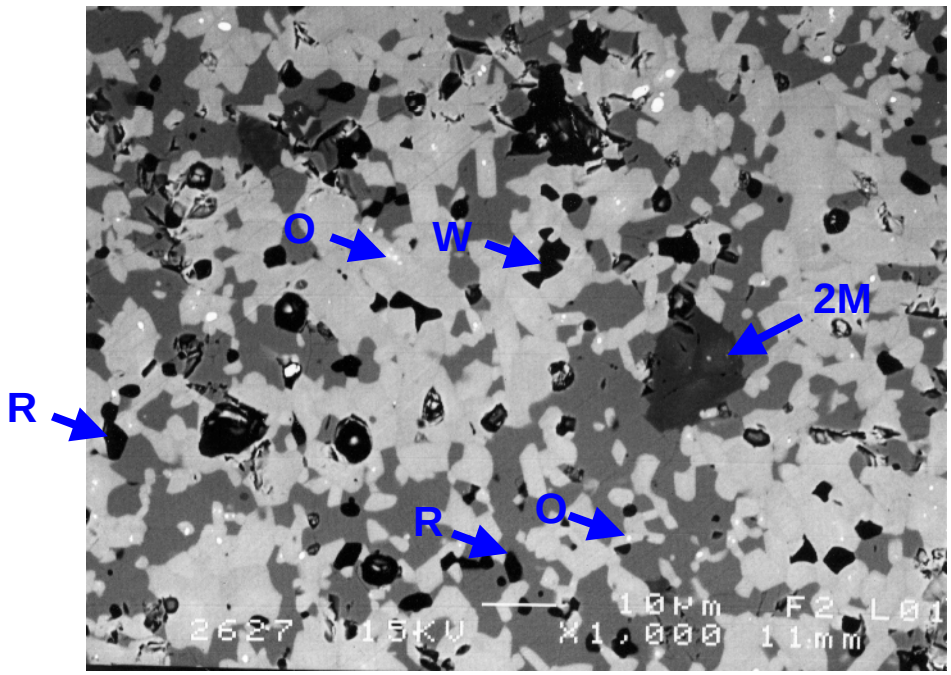
SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-12 - Th/U-DOPED BRANNERITE-RICH CERAMIC

D APPENDIX D: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-12 - TH/U-DOPED BRANNERITE-RICH CERAMIC

D.1 SEM IMAGES



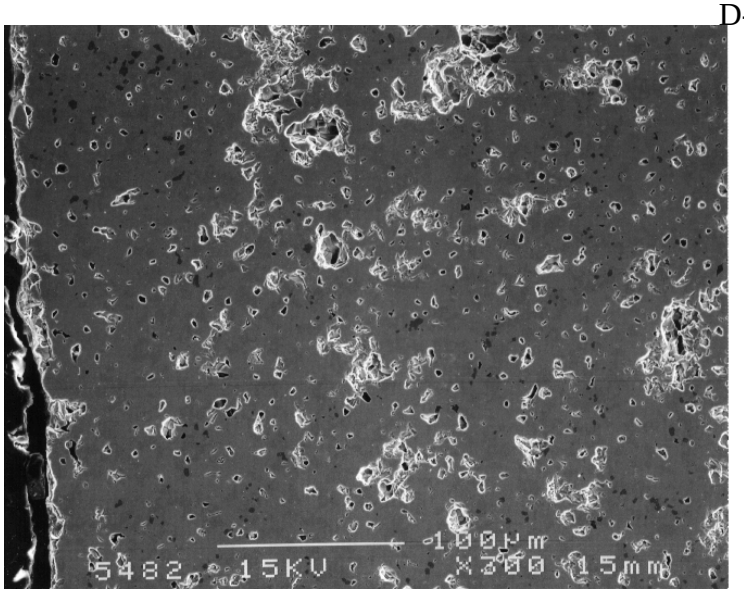
(a)



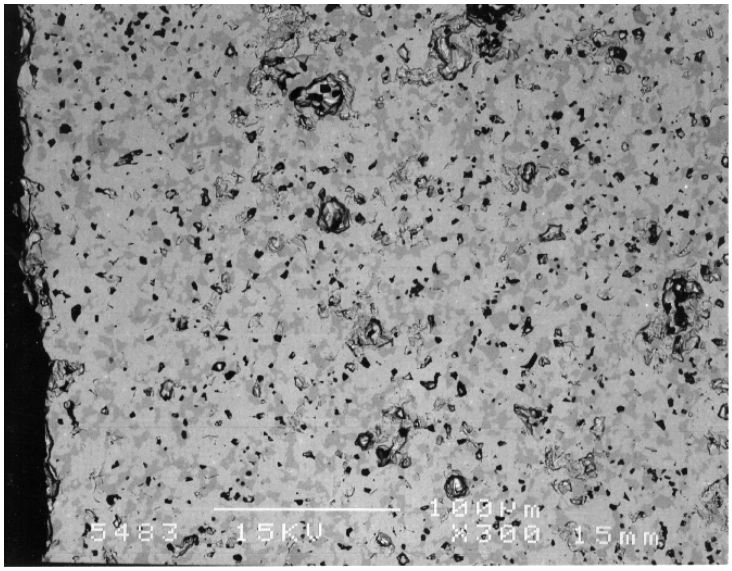
(b) 10 µm.

Figure D-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980141 (composition B1-12, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours. The matrix is a mixture of pyrochlore (mid-grey phase) and Th/U-brannerite (light-grey phase). Also present are a trace of 2M zirconolite (2M), Hf-doped rutile (R, dark-grey), ThO_2-UO_2 (O, white), a few (< 1 vol. %) whitlockite grains (W) and

(a)



(b)



(c)

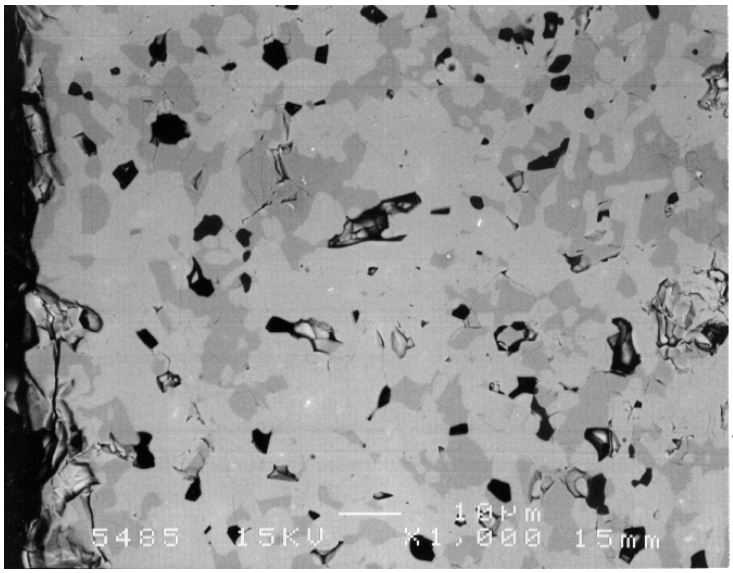
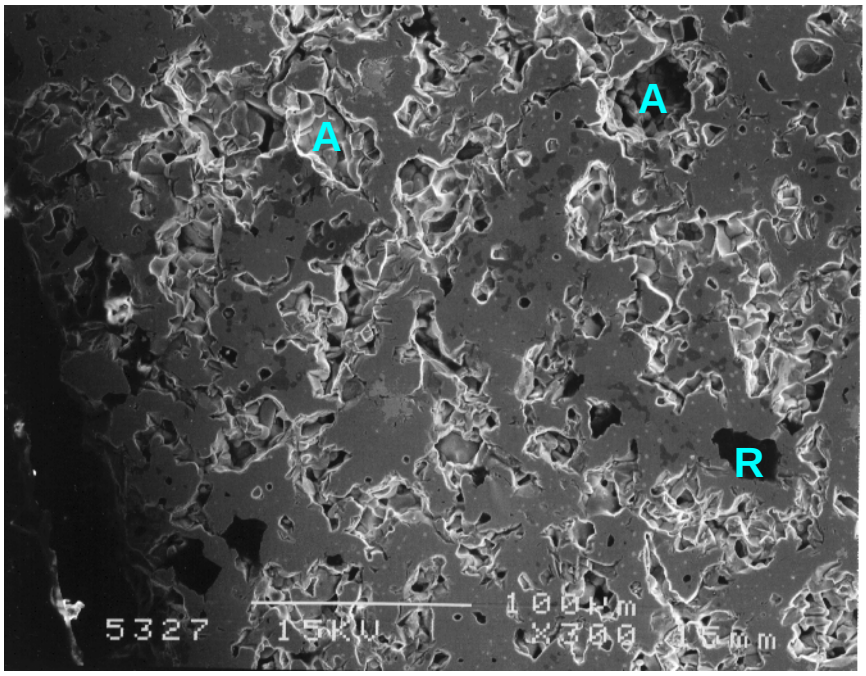
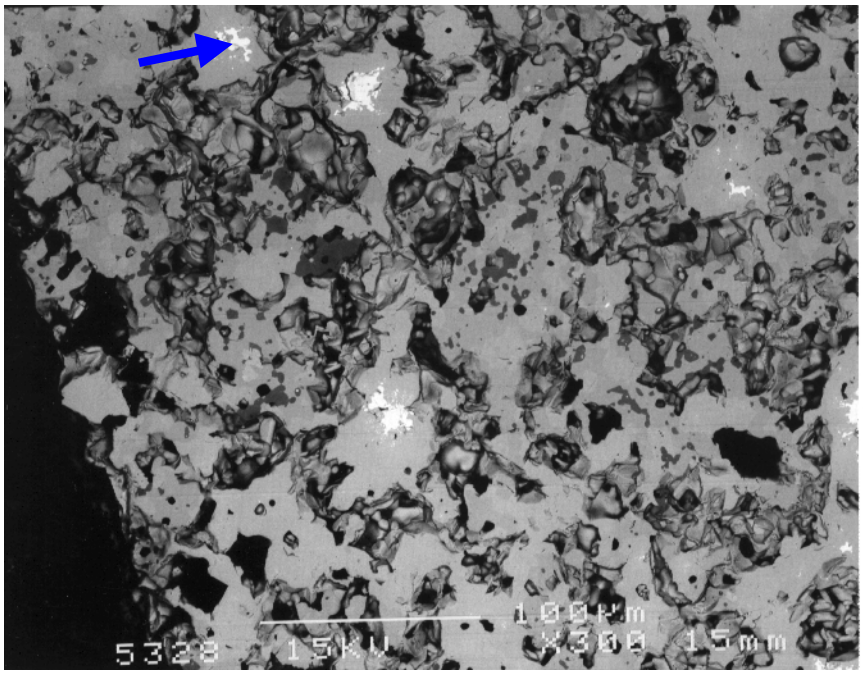


Figure D-2: (a) Secondary electron micrograph and (b) and (c) backscattered electron micrographs of mws990444 (composition B1-12, oxide-route, wet-milled 16 hours, sintered at 1350°C in air for 4 hours. The matrix is a mixture of pyrochlore (mid-grey phase) and Th/U-brannerite (light-grey phase). Also present are Hf-doped rutile (dark-



(a)



(b)

Figure D-3: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws99-0529 (composition B1-12, oxide-route, dry-milled 16 hours, sintered at 1350°C in air for 4 hours. The matrix is a mixture of pyrochlore (mid-grey phase) and Th/U-

(a)

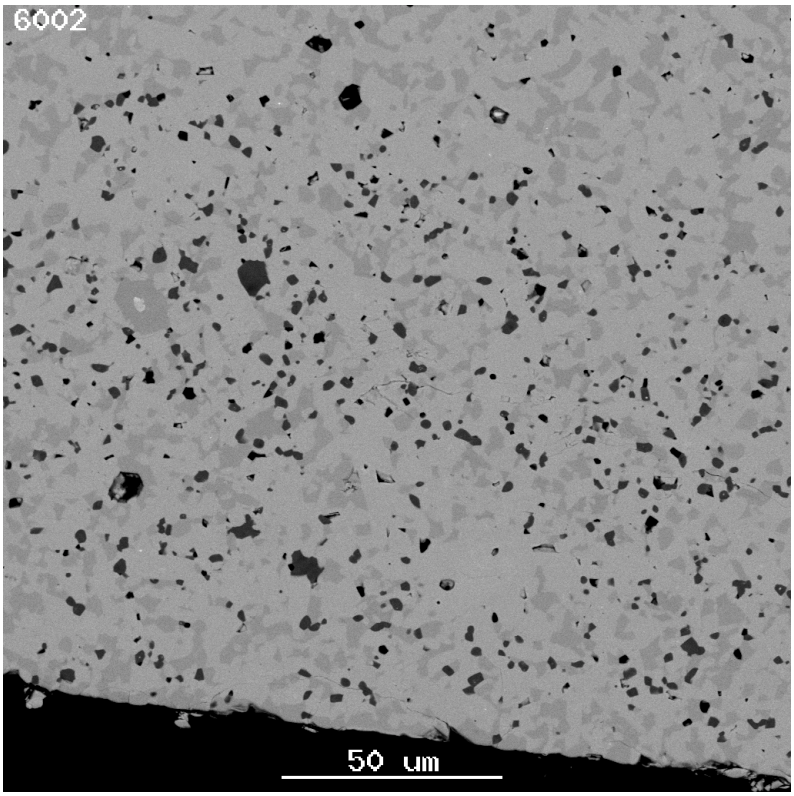
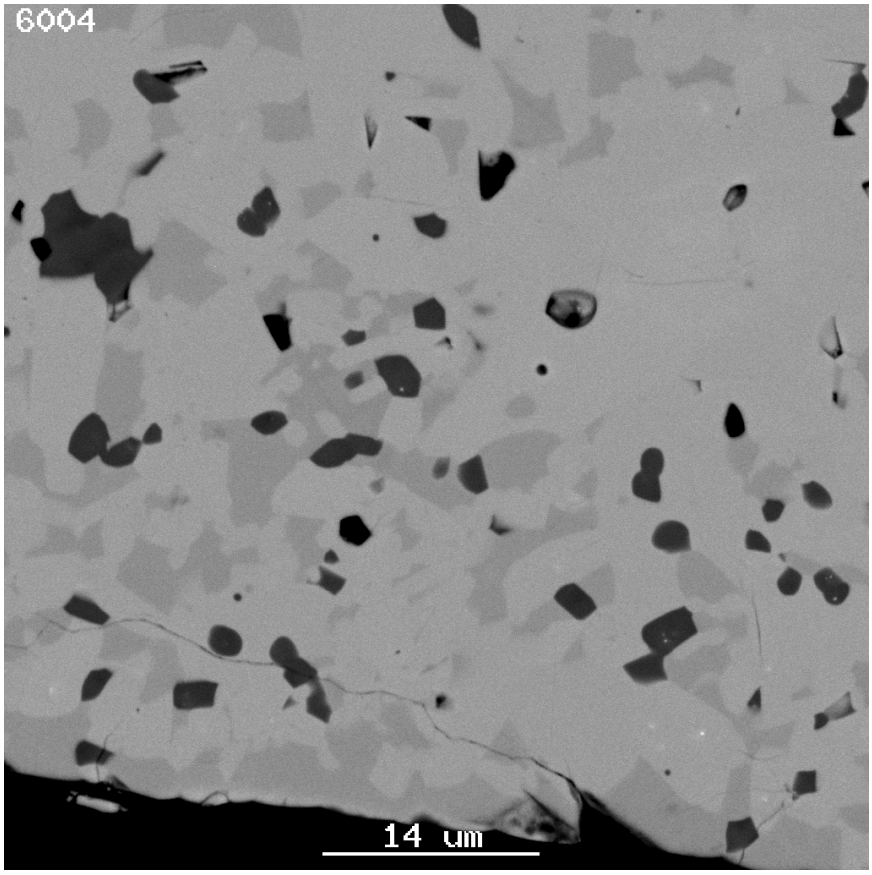
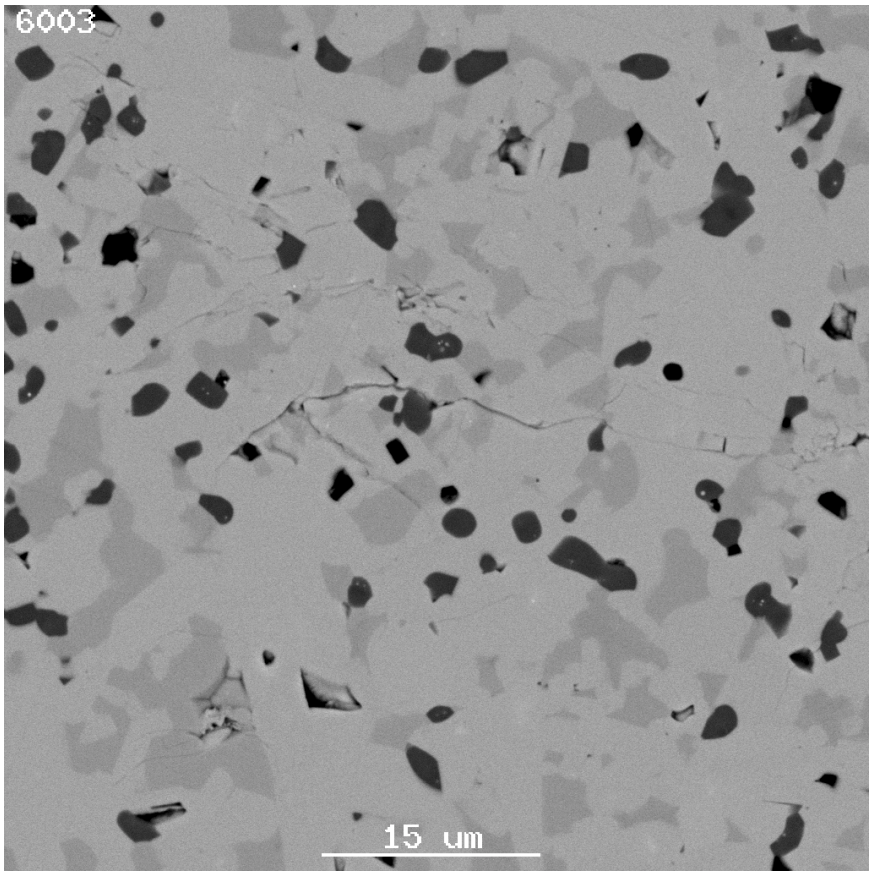


Figure D-4: (a), (b) and (c) backscattered electron micrographs of mws99-0604 (composition B1-12, oxide-route, attrition milled, sintered at 1350°C in air for 4 hours). Micrograph (b) shows the exterior of the pellet and (c) the interior of pellet. The sample consists of a matrix of pyrochlore (mid-grey) and Th/U-brannerite (light-grey) with some (< 1 vol. %) ThO_2-UO_2 (white spots) inside brannerite grains, rutile (dark-grey) and porosity (black).

(b)



(c)



D.2 EDS ANALYSES

Table D-1: EDS analyses of phases (number of cations) in the pellet mws980141 made from composition, B1-12, Th/U-doped oxide-rou batch, which was wet-milled ball milled for 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.

Sample No.	**mws980145**				
	pyrochlore	**2M zirconolite**	**brannerite**	**Th/U-Oxide**	**Rutile**
~ abundance (vol. %)	55-65	2	30 - 40	< 1	3-5
Element					
oxygen	7	7	6	2	2
Ca	0.97	0.80	0.05	0.07	
Gd	0.28	0.13	0.12	0.06	
Hf	0.27	0.88	0.14	0.01	0.08
U $^{\$}$	0.42	0.07	0.49	0.83	0.005
Th	0.13	0.02	0.27	0.04	
Ti	1.99	1.91	1.99	0.03	
Al		0.16			
Total	4.05	3.97	3.06	1.04	1.05

$ The uranium is taken to be U^{4+} for analysis purposes.

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EI system

The standard error in the individual measurements is ~ 1 %.

Table D-2 - EDS analyses of phases (number of cations) found at the exterior and interior of the pellet mws990444 (B1-12, brannerite-rich composition, wet ball milled for 16 hours) that had been sintered in air at 1350°C for 4 hours. The exterior EDS measurements we taken within the outer 20 μm of the pellet and the interior EDS measurements were taken > 100μm from the outside of the pellet.

	Interior				Exterior			
Phase	**pyrochlore**	**brannerite**	**Th/U-oxide &**	**rutile**	**pyrochlore**	**brannerite**	**Th/U-oxide &**	**rutil**
~ abundance (vol. %)	45-55	45-55	< 1	3-5	45-55	45-55	< 1	3
Element								
oxygen	7	6		2	7	6		2
Ca	1.15	0.11		0.004	1.15	0.11		0.00
Gd	0.19	0.11		0.001	0.18	0.13		0.00
Hf	0.27	0.15		0.09	0.27	0.15		0.10
Th	0.10	0.29		0.002	0.10	0.26		0.00
U $	0.53	0.41		0.008	0.54	0.43		0.00
Ti	1.89	2.00		0.90	1.89	2.01		0.89
Total	4.12	3.08		1.00	4.13	3.09		1.00

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
& Too small to analyse accurately
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the individual measurements is ~ 1 %.

Table D-3 - EDS analyses of phases (number of cations) found at the exterior and interior of the pellet mws99-0529 (B1-12, brannerite-rich composition, dry ball milled for 16 hours) that had been sintered in air at 1350°C for 4 hours.

	Interior				Exterior			
Phase	**pyrochlore**	**brannerite**	**Th/U-oxide**	**rutile**	**pyrochlore**	**brannerite**	**Th/U-oxide**	**ru**
~ abundance (vol. %)	45-55	45-55	1 - 3	3-7	45-55	45-55	1 - 3	3
Element								
oxygen	7	6	2	2	7	6	2	
Ca	1.11	0.08 – 0.11	0.06 – 0.08	0.005	1.17	0.08 – 0.11	0.05	0.
Gd	0.18 – 0.22	0.11	0.07	0.001	0.19	0.11 – 0.14	0.05	
Hf	0.27	0.13	0.005 – 0.015	0.12	0.25	0.12 – 0.14	0.009 – 0.014	0.
Th	0.07 – 0.09	0.29 – 0.41	0.55 – 0.64	0.001	0.09	0.25 – 0.28	0.64 – 0.71	0.
U [$]	0.53 - 0.56	0.36 – 0.42	0.26 – 0.32	0.008	0.54	0.37 – 0.46	0.21 – 0.28	0.
Ti	1.89	1.97 - 2.02	0.006 – 0.012	0.87	1.89	1.98 – 2.01	0.001 – 0.009	0.
Total	4.10 [+]	3.07 [+]	1.05 [+]	1.01	4.13	3.06 - 3.09 [+]	1.04 [+]	1.

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

\+ Despite compositional variations the elements always added up to this total.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system. The standard error in the individual measurements is ~ 1 %.

Table D-4 - EDS analyses of phases (number of cations) found at the exterior and interior of the pellet mws99-0604 (B1-12, brannerite-rich composition, attrition milled) that had been sintered in air at 1350°C for 4 hours. The exterior EDS measurements were taken within the outer 20 μm of the pellet and the interior EDS measurements were taken > 100μm from the outside of the pellet.

	Interior					Exterior			
Phase	**pyrochlore**	**brannerite**	**Thoria &**	**Hafnia &**	**rutile**	**pyrochlore**	**brannerite**	**Thoria &**	**rutil**
~ abundance (vol. %)	45-55	45-55	< 1	< 1	5	45-55	45-55	< 1	5
Element									
oxygen	7	6			2	7	6		2
Ca	0.80 - 1.05	0.09 – 0.11			0.003	1.10	0.10		0.00
Gd	0.19	0.14			0.001	0.21	0.13 – 0.16		
Hf	0.25 - 0.34	0.15 – 0.16			0.11	0.26	0.15		0.11
Th	0.09 – 0.17	0.25 – 0.36			0.002	0.11	0.25 0.28		0.00
U $	0.46 – 0.50	0.34 – 0.41			0.006	0.50	0.40 – 0.43		0.00
Ti	1.94 - 2.04	2.00			0.88	1.92	2.01		0.89
Total	3.94 – 4.07	3.09 +			1.00	4.11	3.09 +		1.00

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
\+ Despite compositional variations the elements always added up to this total.
& Too small to analyse accurately.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the individual measurements is ~ 1 %.

D.3 XRD RESULTS

Table D-5: A summary of the XRD results for samples made of composition B1-12 (Th/U/Hf-brannerite-rich ceramic).

Description - Processing Route			
Route/Milling/Sint. Temp. (°C)/ Sint. atmosphere/Sample No.	**XRD Description**	**XRD File Name.**	**Phases Present**
oxide/wet ball/1350/Ar/ mws990437	As fired pellet surface top	t1497	pyrochlore, brannerite, rutile
	As fired pellet surface bottom	t1503	pyrochlore, brannerite, rutile
	Powder with W reference.	t1802	pyrochlore, brannerite, rutile, tungsten
oxide/wet ball/1350/air/ mws990444	As fired pellet surface top	t1597	pyrochlore, brannerite, rutile
	As fired pellet surface bottom	t1621	pyrochlore, brannerite, rutile
	Ground surface of pellet	t1742	pyrochlore, brannerite, rutile
	Powder with W reference.	t1863	pyrochlore, brannerite, rutile, tungsten
oxide/dry ball/1350/air/ mws99-0529	Ground surface of pellet	s15954	pyrochlore, brannerite, rutile
oxide/wet attrition/1350/air/ mws00-0604	As fired pellet surface top	s16205	pyrochlore, brannerite, rutile
	Ground surface of pellet	s16196	pyrochlore, brannerite, rutile
	Powder with W reference standard	t2559	pyrochlore, brannerite, tungsten, possibly rutile

The above Table contains a list of the raw XRD data files. Note that those starting with t are Scintag Diffractometer files (Cu K-alpha radiation) and those starting with S are Siemens D500 Diffractometer data files (Co K-alpha). The broad low angle peak ~ 15 - 25° (2 theta) in some of the patterns is from the resin used to mount the samples. The raw data files are on the enclosed computer disk.

s*.raw files are Siemens D500 files.

t*.raw files are Scintag raw files using DMSNT Version 1.3 (Diffraction Management System) for Microsoft Windows NT 4.0, t*.txt are text files of Scintag files, t*.rd are Scintag files exported as older version Scintag binary files.

D.3.1 Oxide-route Wet Ball Milled Sample Fired at 1350°C in Ar

The XRD patterns of the top and bottom of the pellet are similar. The XRD pattern of the powdered sample is similar to that of the solid surfaces.

D.3.2 Oxide-route Wet Ball Milled Sample Fired at 1350°C in Air

The XRD patterns of the top and bottom of the pellet are similar. The ground surface and powder XRD patterns are different to those of the top and bottom surfaces; the brannerite peaks are more intense.

D.3.3 Oxide-route Dry Ball Milled Sample Fired at 1350°C in Air

The XRD pattern is to the wet milled samples above (preceding section), except that the rutile peaks appear to be more intense

D.3.4 Oxide-route Attrition Milled Sample Fired at 1350°C in Air

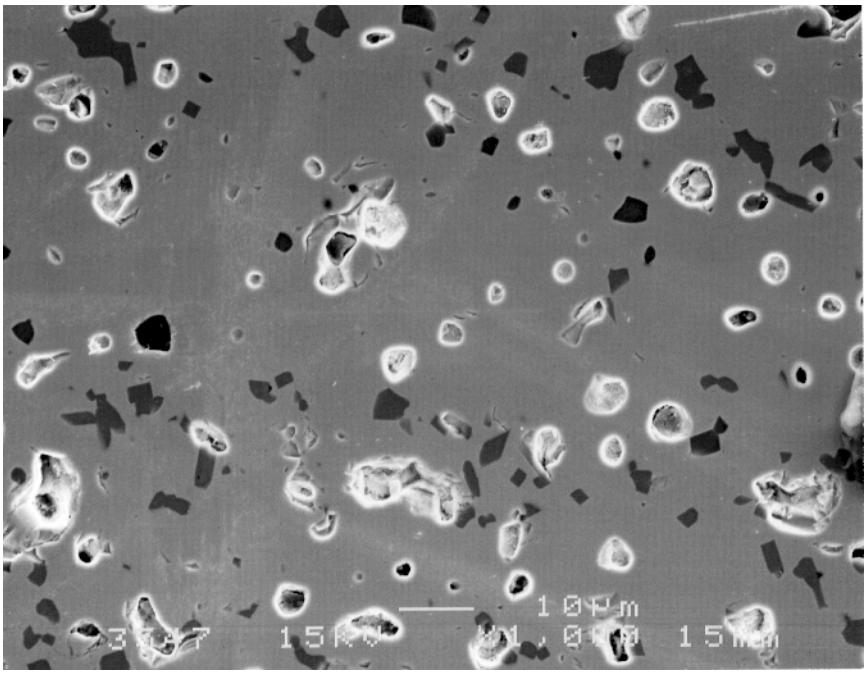
The results are very similar to those of the wet ball milled sample sintered in air (see D.3.2 above). The XRD pattern of the ground surface of the pellet has more intense brannerite peaks than the XRD pattern of the exterior surface.

APPENDIX E

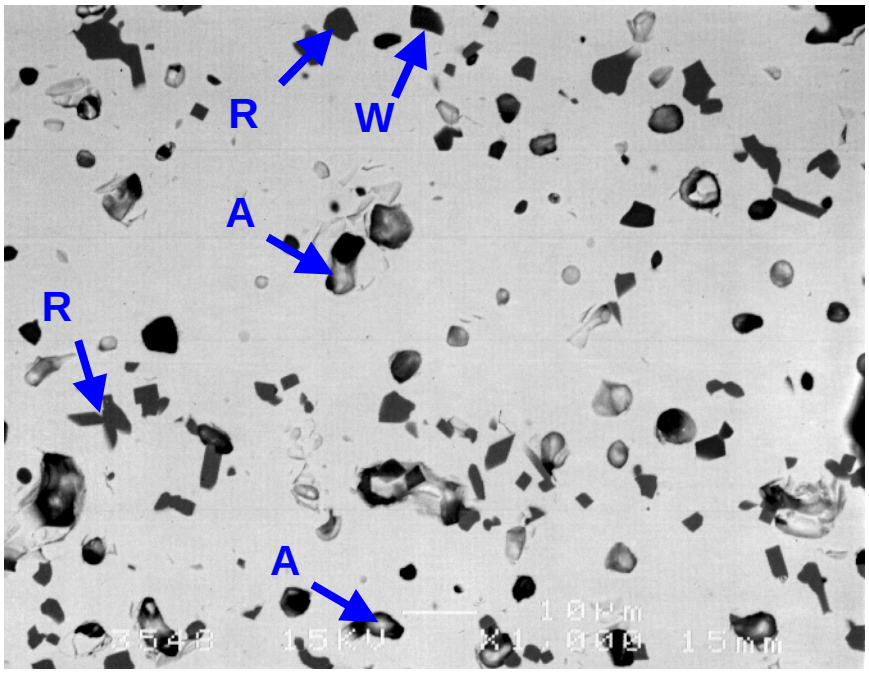
SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-14 - Th/U-DOPED “NOMINALLY” 10 % PEROVSKITE CERAMIC

E. APPENDIX E: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-14 - TH/U-DOPED “NOMINALLY” 10 % PEROVSKITE CERAMIC

E.1 SEM IMAGES



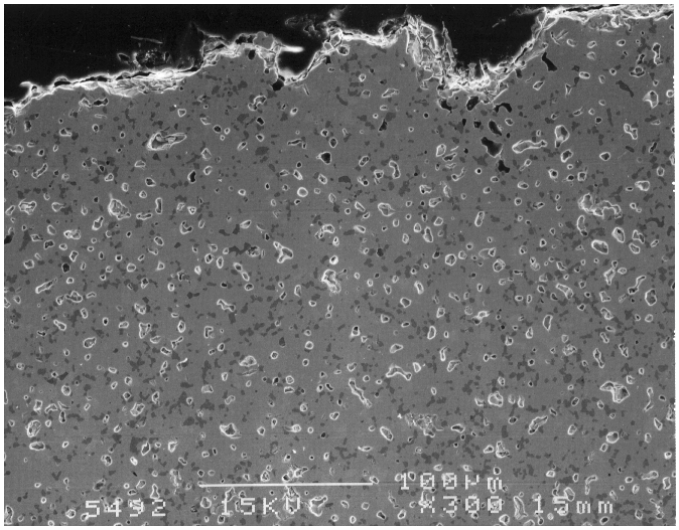
(a)



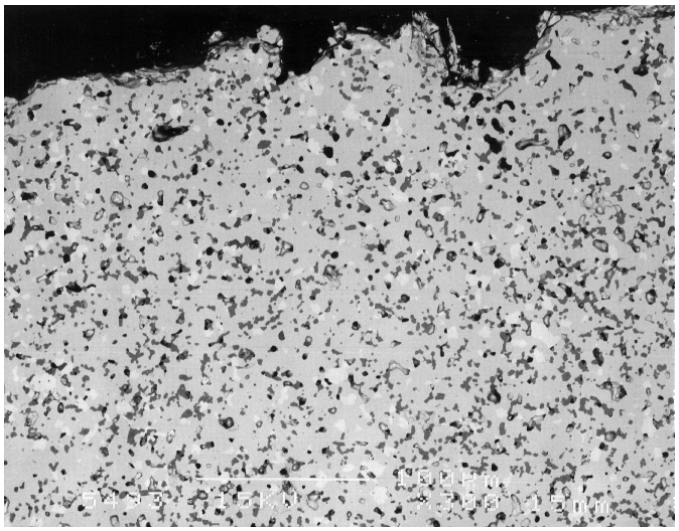
(b) 10 µm.

Figure E-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980258 (composition B1-14, oxide-route, wet ball milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore, with some Hf-doped rutile (R) and porosity (A). Some whitlockite (W, dark grey blocky grains) is also present. Brannerite

(a)



(b)



(c)

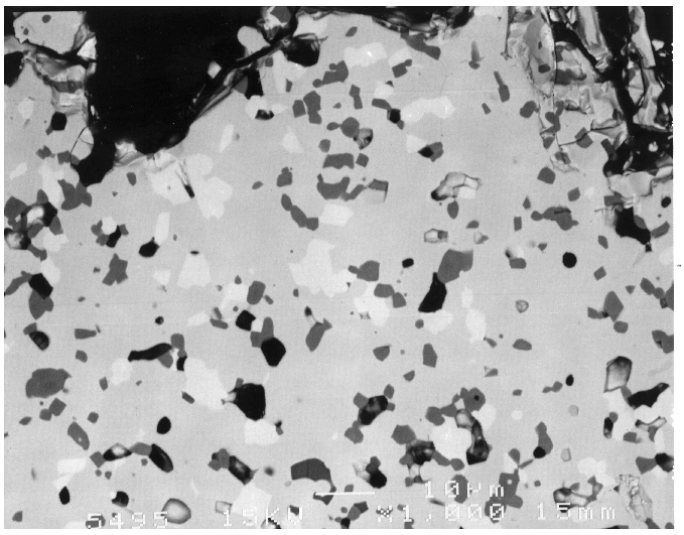


Figure E-2: (a) A secondary electron micrograph; (b) and (c) backscattered electron micrographs of mws990445 (composition B1-14, oxide-route, wet ball milled 16 hours, sintered at 1350°C in air for 4 hours). The matrix is pyrochlore, with Hf-doped rutile (dark–grey grains in (a)), brannerite (light grains in (b) and (c)) and porosity (see (a)).

E.2 EDS ANALYSES

Table E-1: EDS analyses of phases (number of cations) in the pellets made from composition B1-14, Th/U-doped oxide-route batch wet milled for 16 hours. Pellets were sintered in Ar at 1350°C for 4 hours.

Sample No.	**mws980258**		
	pyrochlore	**rutile**	**Whitlockite**
~ abundance (vol. %)	93 - 95	5 - 7	<< 1
Element			
oxygen	7	2	8
Ca	0.90	0.003	2.63
Gd	0.19		0.13
Hf	0.25	0.06	
U [$]	0.34	0.002	0.002
Th	0.23	0.001	0.01
Ti	2.08	0.94	0.02
P [*]			2.00
Mg [#]			0.11
Total	4.00	1.00	4.91

$ The uranium is taken to be U^{4+} for analysis purposes.

* From anatase raw material

\# Processing/raw material impurity, source unknown

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

The standard error in the individual measurements is ~ 1 %.

Table E-2 - EDS analyses of phases (number of cations) found at the exterior and interior of the pellet mws990445 (B1-14, nominally ~ 10 % perovskite composition) that had been sintered in air at 1350°C for 4 hours. The exterior EDS measurements were taken within the outer 20 μm of the pellet and the interior EDS measurements were taken > 100μm from the outside of the pellet.

	Interior			Exterior		
Phase	**pyrochlore**	**brannerite**	**rutile**	**pyrochlore**	**brannerite**	**rutile**
~ abundance (vol. %)	80-90	5-10	5-10	80-90	5-10	5-10
Element						
oxygen	7	6	2	7	6	2
Ca	1.07	0.08	0.009	1.06	0.08	0.005
Gd	0.21	0.09	0.001	0.21	0.10	
Hf	0.23	0.12	0.07	0.22	0.12	0.10
Th	0.20	0.48	0.002	0.21	0.44	0.002
U [$]	0.38	0.28	0.007	0.38	0.30	0.002
Ti	1.99	2.01	0.92	2.00	2.02	0.89
Total	4.09	3.06	1.01	4.09	3.06	1.01

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the individual measurements is ~ 1 %.

E.3 XRD RESULTS

Table E-3: A summary of the XRD results for samples made of composition B1-14 ("nominally" 10 % perovskite Th/U/Hf-ceramic).

Description - Processing Route			
Route/Milling/Sint. Temp. (^{o}C)/ Sint. atmosphere/Sample No.	**XRD Description**	**XRD File Name.**	**Phases Present**
oxide/wet ball/1350// mws990438	As fired pellet top surface	t1498	pyrochlore, rutile
	As fired pellet bottom surface	t1504	pyrochlore, , rutile
	Powder with W reference.	t1620	pyrochlore, , rutile, tungsten
oxide/wet ball/1350/air/ mws990445	As fired pellet top surface	t1598	pyrochlore, brannerite, rutile
	As fired pellet bottom surface	t1622	pyrochlore, brannerite, rutile
	Ground surface of pellet	t1743	pyrochlore, brannerite, rutile
	Powder with W reference.	t1864	pyrochlore, brannerite, rutile, tungsten

The above Table contains a list of the raw XRD data files. Note that those starting with t are Scintag Diffractometer files (Cu K-alpha radiation) and those starting with S are Siemens D500 Diffractometer data files (Co K-alpha). The broad low angle peak ~ 15 - 25° (2 theta) in some of the patterns is from the resin used to mount the samples. The raw data files are on the enclosed computer disk.

s*.raw files are Siemens D500 files.

t*.raw files are Scintag raw files using DMSNT Version 1.3 (Diffraction Management System) for Microsoft Windows NT 4.0, t*.txt are text files of Scintag files, t*.rd are Scintag files exported as older version Scintag binary files.

E.3.1 Oxide-route Wet Ball Milled Sample Fired at 1350^{o}C in Ar

All the XRD patterns are similar and show pyrochlore and rutile. Brannerite is absent.

E.3.2 Oxide-route Wet Ball Milled Sample Fired at 1350^{o}C in Air

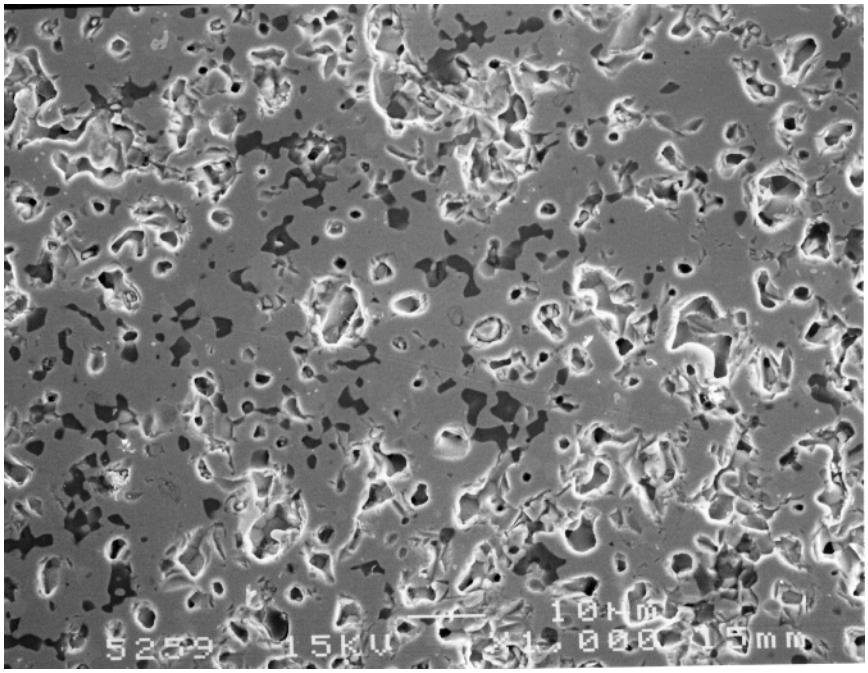
All the XRD patterns are similar. This sample contains brannerite as well as pyrochlore and rutile.

APPENDIX F

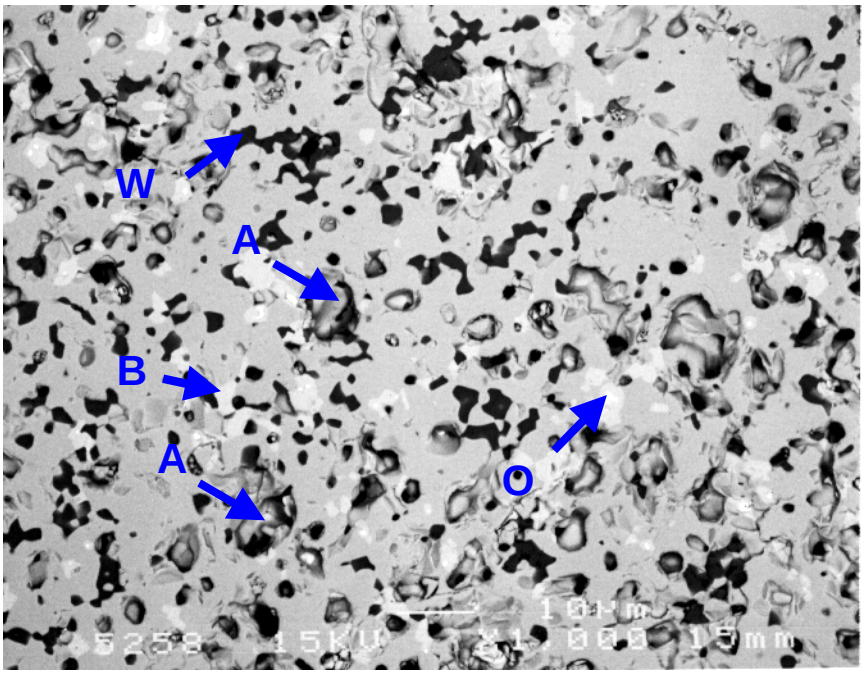
SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-16 - Th/U-DOPED ~ 10 % PHOSPHATE-DOPED CERAMIC

F. APPENDIX F: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-16 - Th/U-DOPED ~ 10 % PHOSPHATE-DOPED CERAMIC

F.1 SEM IMAGES

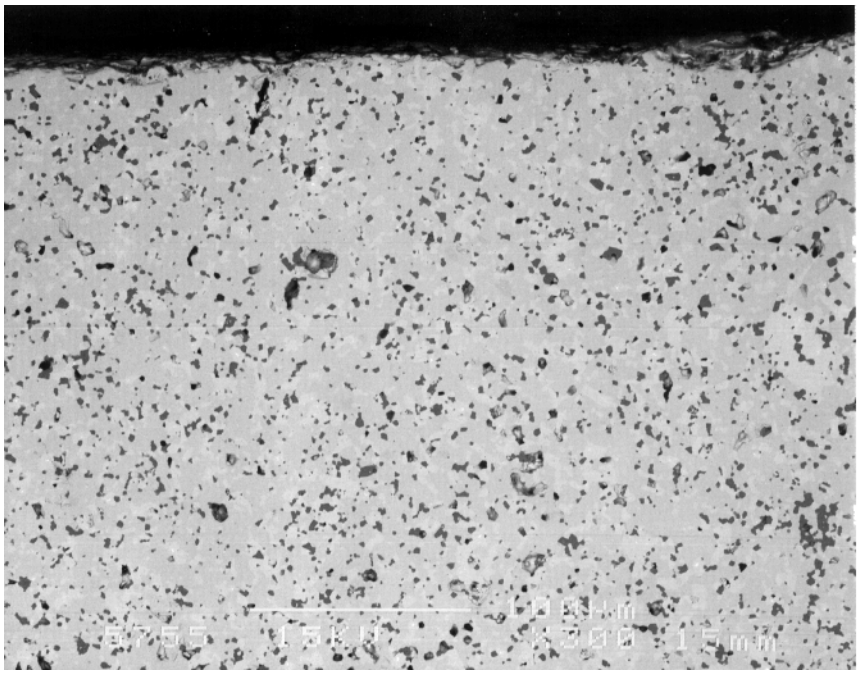


(a)

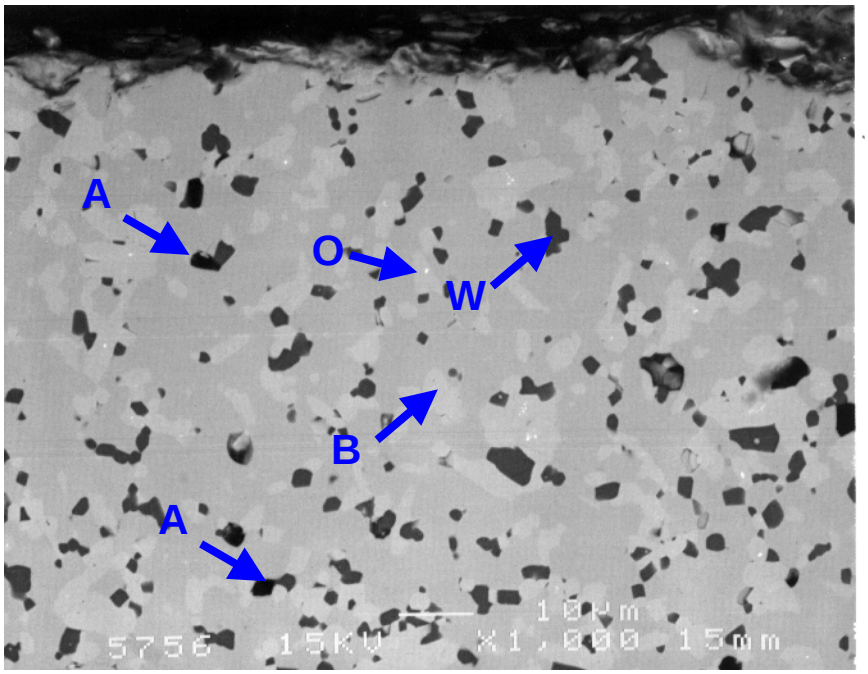


(b) — 10 µm.

Figure F-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980270 (composition B1-16, oxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore, with some brannerite (B, light grey grains)



(a) 10 μm.



(b) 10 μm.

Figure F-2: (a) and (b) backscattered electron micrographs of mws990446 (composition B1-16, oxide-route, wet-milled 16 hours, sintered at 1350°C in air for 4 hours). The matrix is pyrochlore, with brannerite (B, light grey grains), a trace of Th/U-oxide (O, white spots inside the brannerite grains) and whitlockite (W, dark-grey grains). Porosity (see (a)) is present. Some rutile is present as fine dark-grey grains, similar in contrast to the whitlockite.

F.2 EDS ANALYSES

Table F-1: EDS analyses of phases (number of cations) in the sample made from composition B1-16, Th/U-doped 16 hour wet ball mille oxide-route batch. Pellets were sintered in Ar at 1350°C for 4 hours.

Sample No.	**mws980270**			
	pyrochlore	**brannerite**	**Whitlockite**	**Th/U-Oxide***
~ abundance (vol. %)	75	15	10	< 1
Element				
oxygen	7	2	8	
Ca	0.86	0.02	2.59	
Gd	0.19	0.04	0.16	
Hf	0.26	0.13		
U $	0.43	0.36-0.44	0.02	
Th	0.24	0.44-0.54	0.02	
Ti	2.00	1.96	0.06	
P			1.98	
Total	3.98	3.02 +	4.84	

* Variable composition across the pellet.

$ The uranium is taken to be U^{4+} for analysis purposes.

\+ Despite compositional variations the elements always added up to this total.

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS syste The standard error in the individual measurements is ~ 1 %.

Table F-2 - EDS analyses of phases (number of cations) found at the exterior and interior of the pellet mws990446 (B1-16, phosphate-doped composition, wet ball milled for 16 hours) that had been sintered in air at 1350°C for 4 hours.

	Core					Edge				
Phase	**pyrochlore**	**brannerite +**	**whitlockite**	**Th/U-Oxide ***	**rutile &**	**pyrochlore**	**brannerite +**	**whitlockite**	**Th/U-Oxide ***	**ruti**
~ abundance (vol. %)	75-85	10 - 15	5 - 10	< 1	< 1	75-85	10 - 15	5 - 10	< 1	<
Element										
oxygen	7	6	8		2	7	6	8		2
Ca	1.11	0.07	2.53			1.09	0.08	2.56		
Gd	0.22	0.10	0.22			0.22	0.13	0.21		
Hf	0.30	0.12	0.01			0.26	0.14			
Th	0.15	0.51	0.02			0.17	0.38	0.02		
U $	0.44	0.27	0.03			0.47	0.36	0.04		
Ti	1.89	1.99	0.08			1.90	1.98	0.01		
P			1.94					2.02		
Total	4.11	3.06	4.84			4.10	3.07	4.84		

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

\+ Brannerite composition is variable across the sample.

& Rutile is present in small quantities but was not analysed.

* Too small to analyse accurately.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

The standard error in the individual measurements is ~ 1 %.

F.3 XRD RESULTS

Table F-3: A summary of the XRD results for samples made of composition B1-16 (nominally 10 % phosphate Th/U/Hf-ceramics).

Description - Processing Route			
Route/Milling/Sint. Temp. (°C)/ Sint. atmosphere/Sample No.	**XRD Description**	**XRD File Name.**	**Phases Present**
oxide/wet ball/1350/Ar/ mws990439	As fired pellet surface top	t1499	pyrochlore, brannerite
	As fired pellet surface bottom	t1505	pyrochlore, brannerite
	Powder with W reference.	t1804	pyrochlore, brannerite, tungsten
oxide/wet ball/1350/air/ mws990446	As fired pellet surface top	t1557	pyrochlore, brannerite
	As fired pellet surface bottom	t1596	pyrochlore, brannerite
	Ground surface of pellet	t1810	pyrochlore, brannerite
	Powder with W reference.	t1865	pyrochlore, brannerite, tungsten

The above Table contains a list of the raw XRD data files taken with a Scintag Diffractometer files (Cu K-alpha radiation). The patterns are from polished surfaces of pellets. The broad low angle peak ~ 15 - 25° (2 theta) in some of the patterns is from the resin used to mount the samples. The raw data files are on the enclosed computer disk.

s*.raw files are Siemens D500 files.

t*.raw files are Scintag raw files using DMSNT Version 1.3 (Diffraction Management System) for Microsoft Windows NT 4.0, t*.txt are text files of Scintag files, t*.rd are Scintag files exported as older version Scintag binary file

F.3.1 Oxide-route Wet Ball Milled Sample Fired at 1350oC in Ar

All the XRD patterns show pyrochlore and brannerite. The patterns are similar except that some of the brannerite peaks appear to be stronger in the pattern of the bottom surface. The powdered pattern is very similar to the pattern of the top surface.

F.3.2 Oxide-route Wet Ball Milled Sample Fired at 1350°C in Air

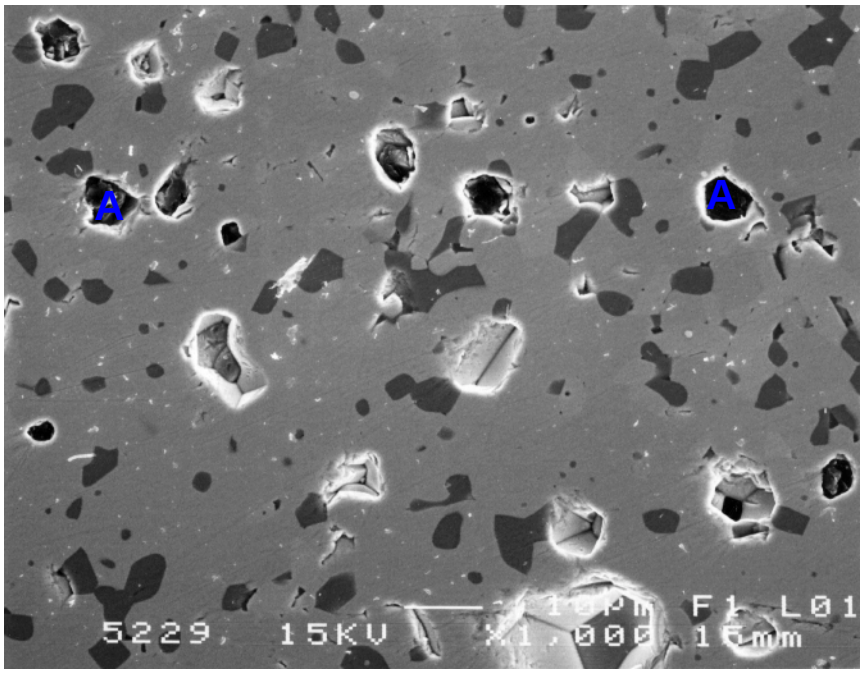
All the XRD patterns are similar. They are also similar to the patterns of the samples sintered in Ar.

APPENDIX G

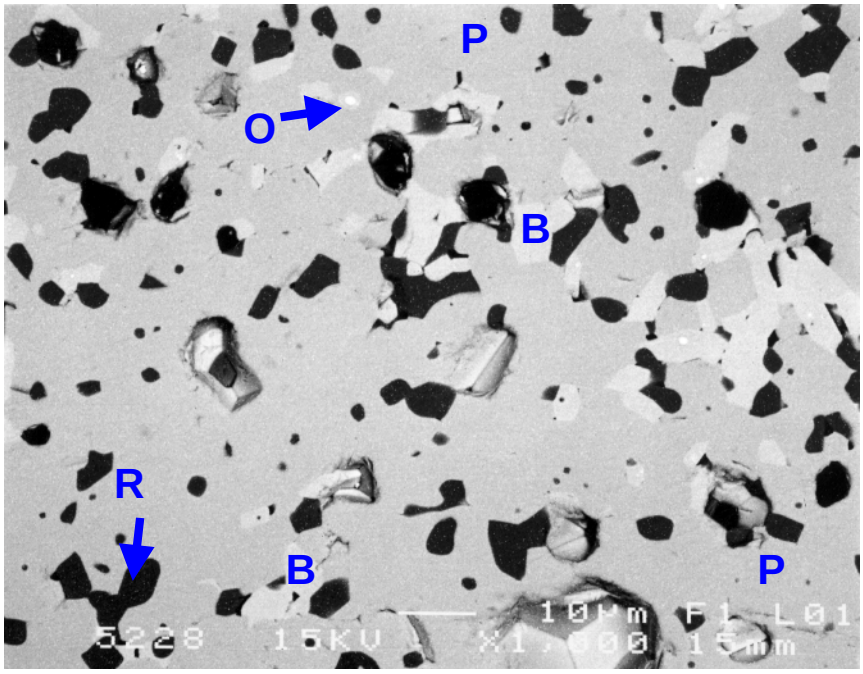
SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-1 - Pu/U-DOPED BASELINE CERAMIC

G. APPENDIX G: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-1 - Pu/U-DOPED BASELINE CERAMIC

G.1 SEM IMAGES



(a)



(b) 10 µm.

Figure G-1: (a) secondary electron micrograph and (b) backscattered electron micrograph of mws980199 (Pu68) (composition B1-1, oxide-route wet- ball milled 16 hours, sintered at 1350°C in Ar for 4 hours). The pellet consists of a matrix of pyrochlore (P), with Pu/U-brannerite (B) grains, Hf-doped rutile (R), PuO_2 (O, white) and porosity (A).

G.2 EDS ANALYSES

Table G-1: EDS analyses of phases (number of cations) in the pellets made from composition B1-1, Pu/U-doped wet-milled oxide-route batch. Pellets were sintered in Ar at 1350°C for 4 hours.

Sample No.	**Pu68**			
	wet-milled oxide			
	Pyrochlore	**brannerite**	**rutile**	**Pu/U-Oxide**
~ abundance (vol. %)	80	15	5	< 1
Element				
oxygen	7	6	2	2
Ca	0.99	0.08	0.001	0.11
Gd	0.24	0.14	0.002	0.08
Hf	0.22	0.11	0.08	0.03
U	0.41	0.53	0.009	0.42
Pu	0.21	0.21	0.001	0.40
Ti	1.98	2.00	0.91	0.04
Total	4.05	3.08	1.00	1.07

$ The uranium is taken to be U^{4+} for analysis purposes.

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system.

The standard error in the individual measurements is ~ 1 %.

G.3 XRD RESULTS

Table G-2: A summary of the XRD results for samples made of composition B1-1 (Pu/U/Hf-baseline ceramic).

Description - Processing Route			
Route/Milling/Sint. Temp. (^{o}C)/ Sint. atmosphere /Sample No.	**XRD Description**	**XRD File Name.**	**Phases Present**
oxide/wet ball/1350/Ar/Pu68	Ground pellet surface top	t1241	pyrochlore, brannerite, rutile

The above Table contains a list of the raw XRD data files. The patterns are from polished surfaces of pellet. The broad low angle peak ~ 15 - 25° (2 theta) in some of the patterns is from the resin used to mount the samples. The raw data files are on the enclosed computer disk.

t*.raw files are Scintag raw files using DMSNT Version 1.3 (Diffraction Management System) for Microsoft Windows NT 4.0, t*.txt are text files of Scintag files, t*.rd are Scintag files exported as older version Scintag binary files.

G.3.1 Oxide-route Wet Ball Milled Sample Fired at 1350°C in Ar

The XRD pattern consists of pyrochlore, brannerite and rutile. This is consistent with the SEM analysis.

G.4 XRD - QUANTITATIVE PHASE ANALYSIS

The following results (Table G-3) were obtained using SIROQUANT software.

Phase	Amount of Phase by Quantitative XRD (%)	Amount of Phase by Image Analysis (%)
Pyrochlore	81.8	79.3
Brannerite	10.8	9.4
Rutile	7.4	11.2

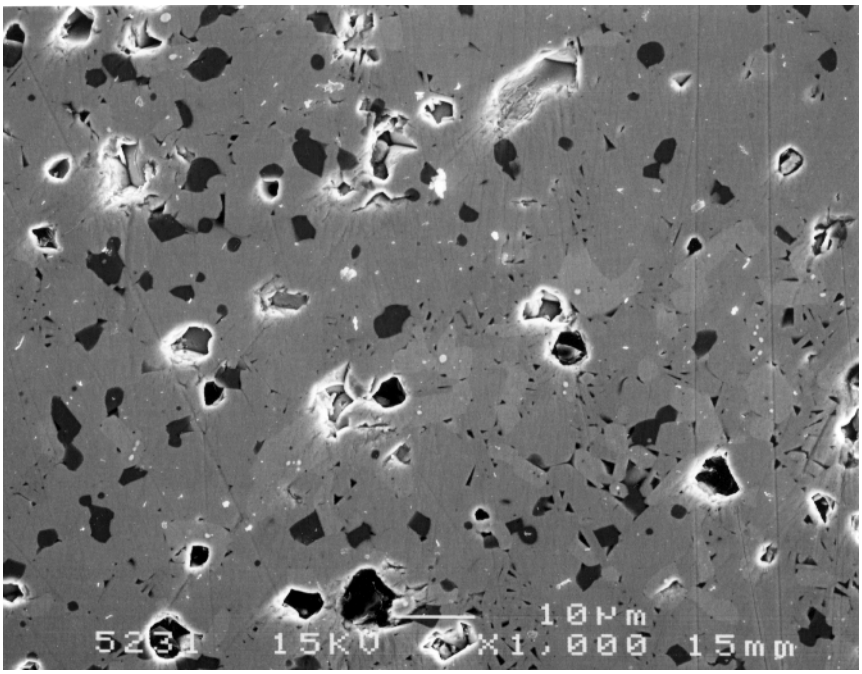
The estimated amount of pyrochlore via both methods was similar. The major difference was that there was much more rutile detected via image analysis. This variation could be caused by a number of factors ranging from the fact that the XRD pattern was taken from a polished solid surface and not a powder to the degree of which the SEM image used for image analysis is representative of the entire sample.

APPENDIX H

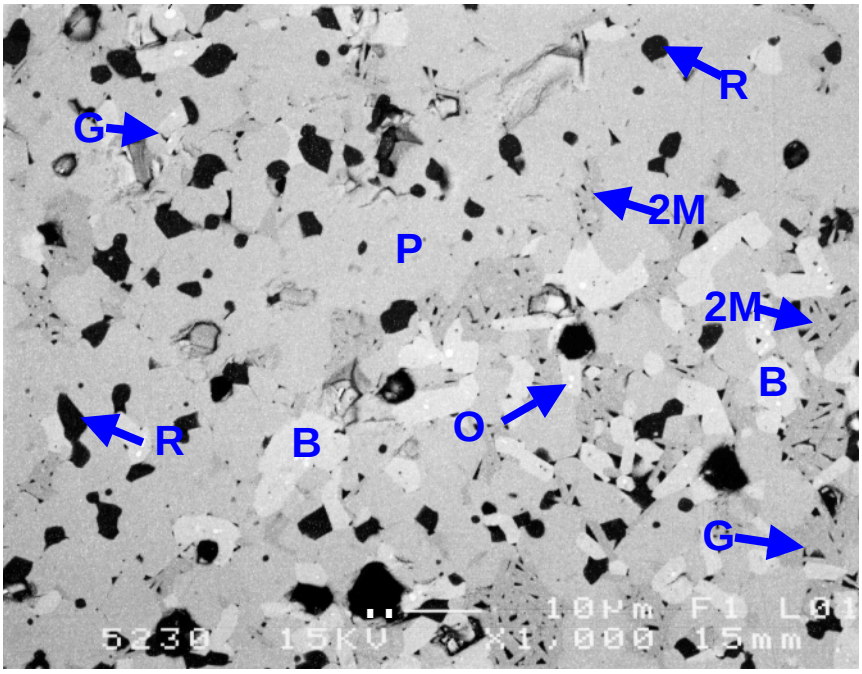
SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION A-7 AND B3-13 - Pu/U-DOPED BASELINE + IMPURITIES CERAMICS

H. APPENDIX H: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION A-7 AND B3-13 - Pu/U-DOPED BASELINE + IMPURITIES CERAMICS

H.1 SEM Images



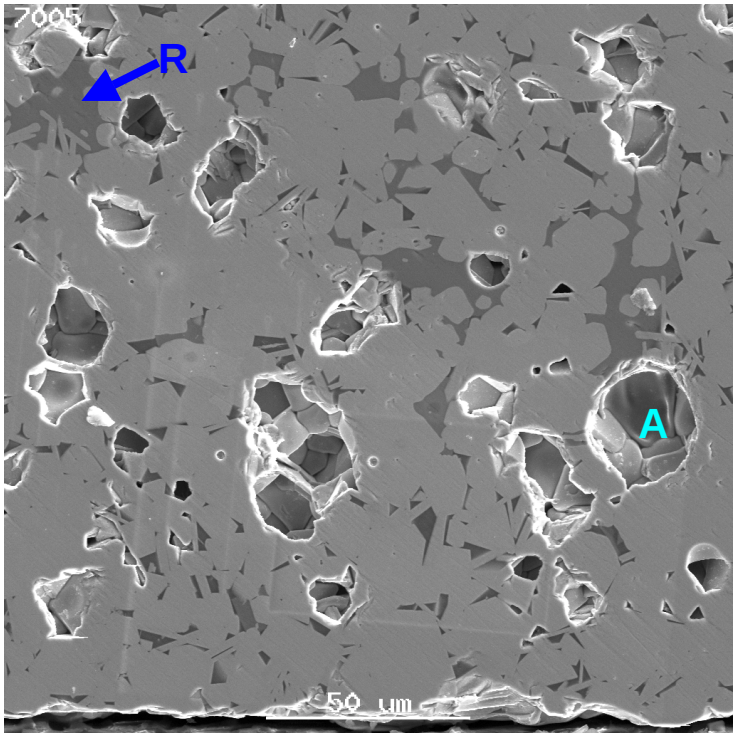
(a)



(b) 10 µm.

Figure H-1: (a) and (b) backscattered electron micrograph of mws980200 (Pu75) (composition A-7, oxide-route wet-milled, sintered at 1325°C in Ar for 4 hours). The pellet consists of a pyrochlore (P), 2M zirconolite (2M), Pu/U-brannerite (B), Hf-doped rutile (R), a silicate intergranular phase (G), PuO_2 (O) and porosity (A).

(a)



(b)

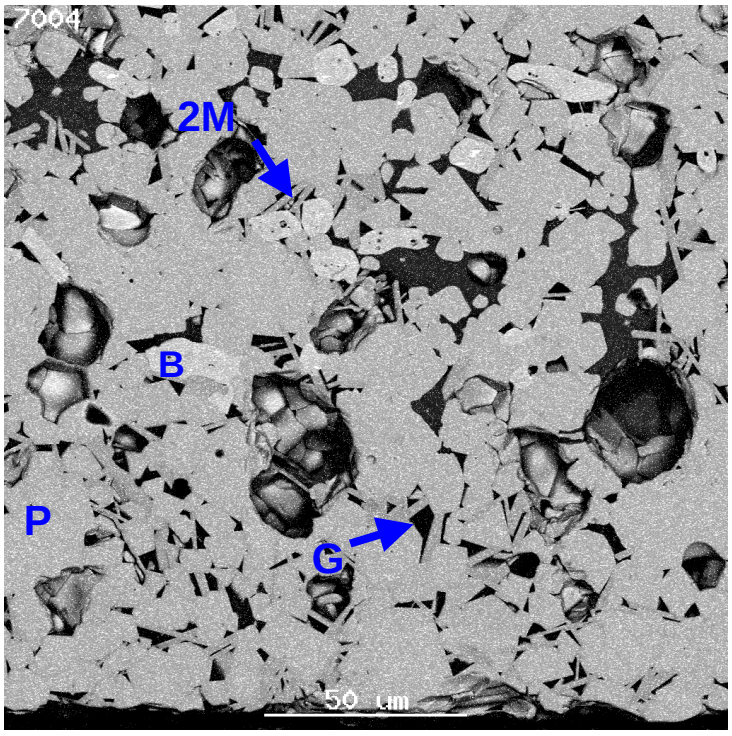
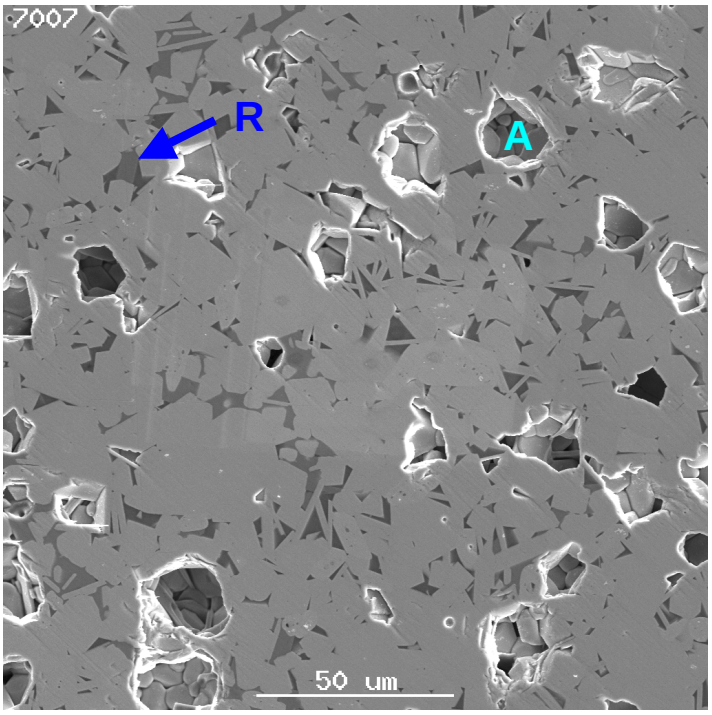


Figure H-2: (a) Secondary electron and (b) backscattered electron micrographs of the bottom of pellet Pu11802 (composition B3-13, oxide-route wet-milled, sintered at 1325°C in Ar for 4 hours). The pellet consists of a pyrochlore (P, matrix), 2M zirconolite (2M, slightly darker and more elongated grains than pyrochlore), Pu/U-brannerite (B, light grey), Hf-doped rutile (R, dark grey), a silicate intergranular phase (G, black), PuO_2 (very small white regions inside some brannerite grains) and porosity (A).

(a)



(b)

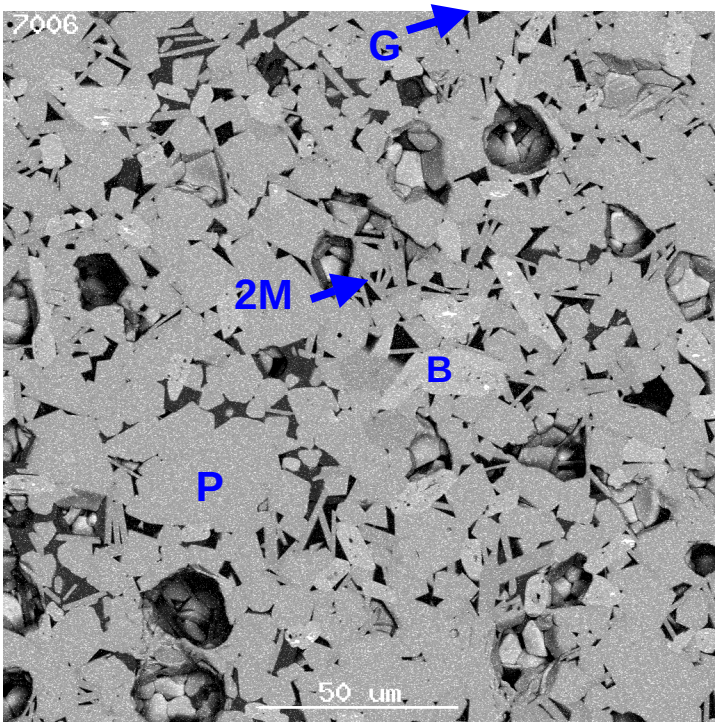
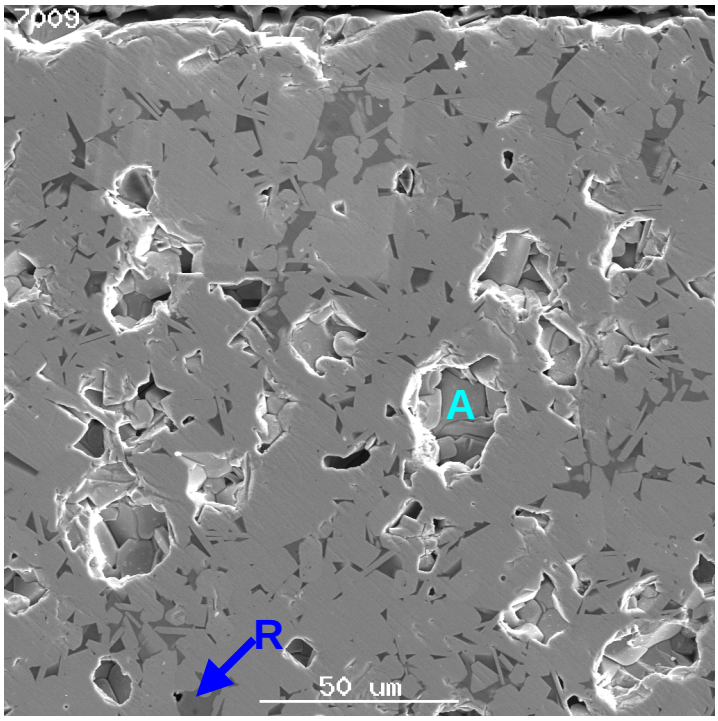


Figure H-3: (a) Secondary electron and (b) backscattered electron micrographs of the middle of pellet Pu11802 (composition B3-13, oxide-route wet-milled, sintered at 1325°C in Ar for 4 hours). The pellet consists of a pyrochlore (P, matrix), 2M zirconolite (2M, slightly darker and more elongated grains than pyrochlore), Pu/U-brannerite (B, light grey), Hf-doped rutile (R, dark grey), a silicate intergranular phase (G, black), PuO_2 (very small white regions inside some brannerite grains) and porosity (A).

(a)



(b)

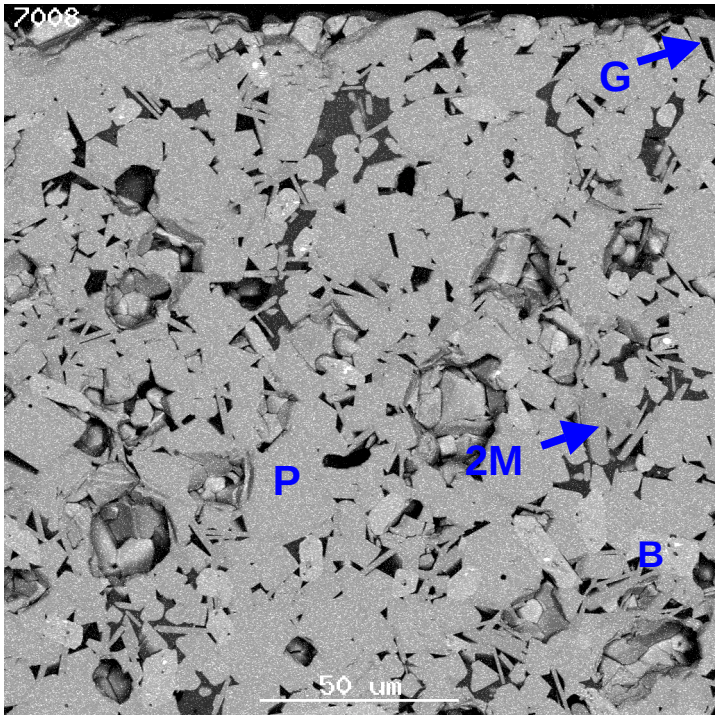
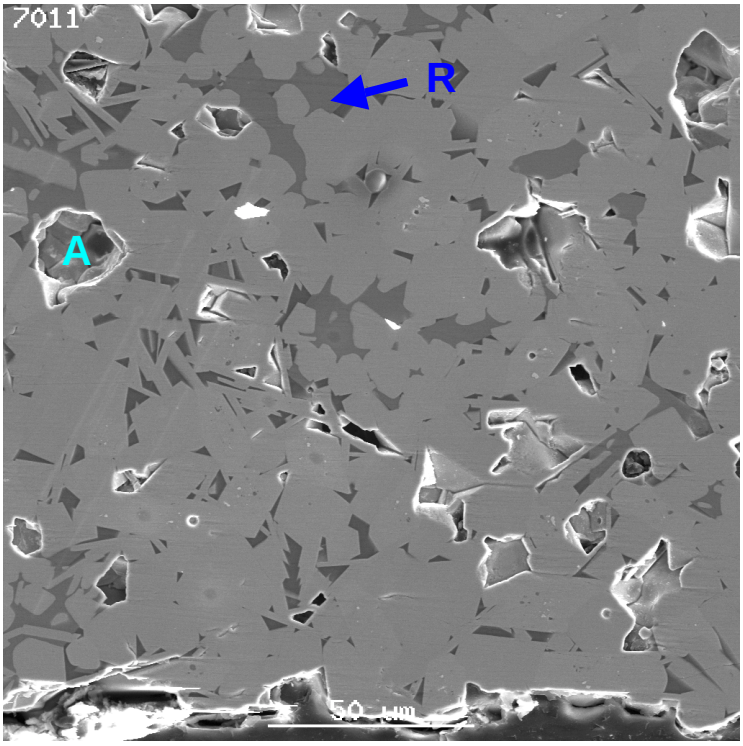


Figure H-4: (a) Secondary electron and (b) backscattered electron micrographs of the top of pellet Pu11802 (composition B3-13, oxide-route wet-milled, sintered at 1325°C in Ar for 4 hours). The pellet consists of a pyrochlore (P, matrix), 2M zirconolite (2M, slightly darker and more elongated grains than pyrochlore), Pu/U-brannerite (B, light grey), Hf-doped rutile (R, dark grey), a silicate intergranular phase (G, black), PuO_2 (very small white regions inside some brannerite grains) and porosity (A).

(a)



(b)

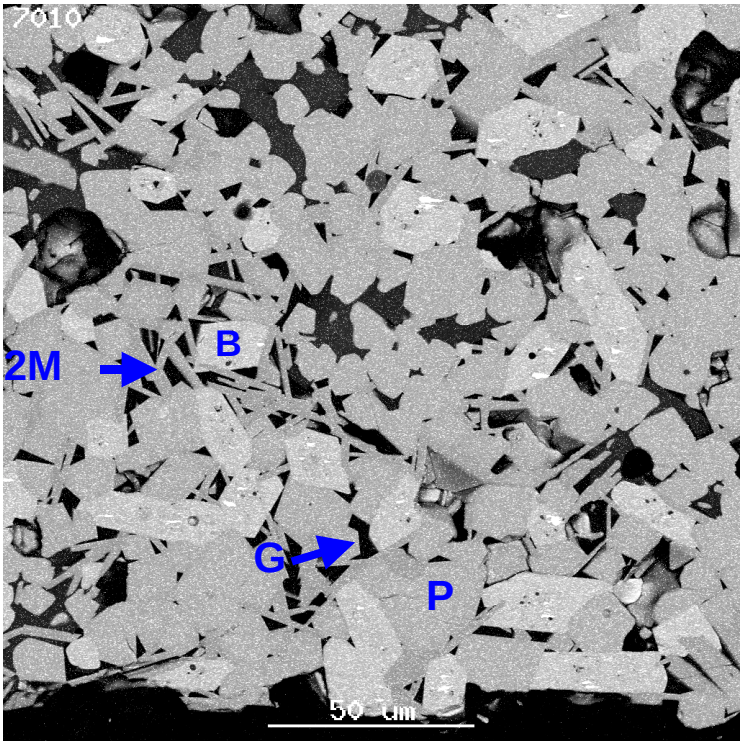
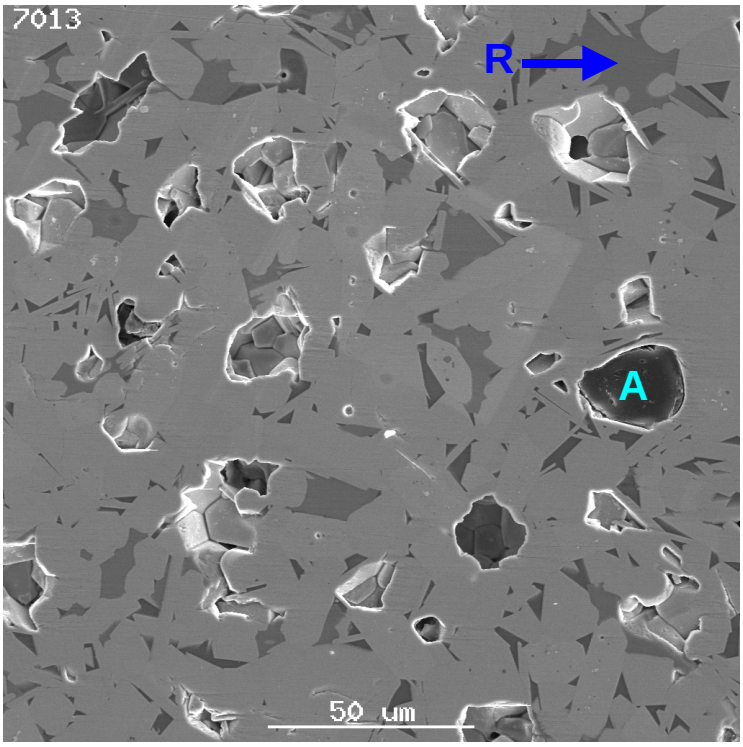


Figure H-5: (a) Secondary electron and (b) backscattered electron micrographs of the bottom of pellet Pu11803 (composition B3-13, oxide-route wet-milled, sintered at 1325°C in air for 4 hours). The pellet consists of a pyrochlore (P, matrix), 2M zirconolite (2M, slightly darker and more elongated grains than pyrochlore), Pu/U-brannerite (B, light grey), Hf-doped rutile (R, dark grey), a silicate intergranular phase (G, black), PuO_2 (very small white regions inside some brannerite grains) and porosity (A).

(a)



(b)

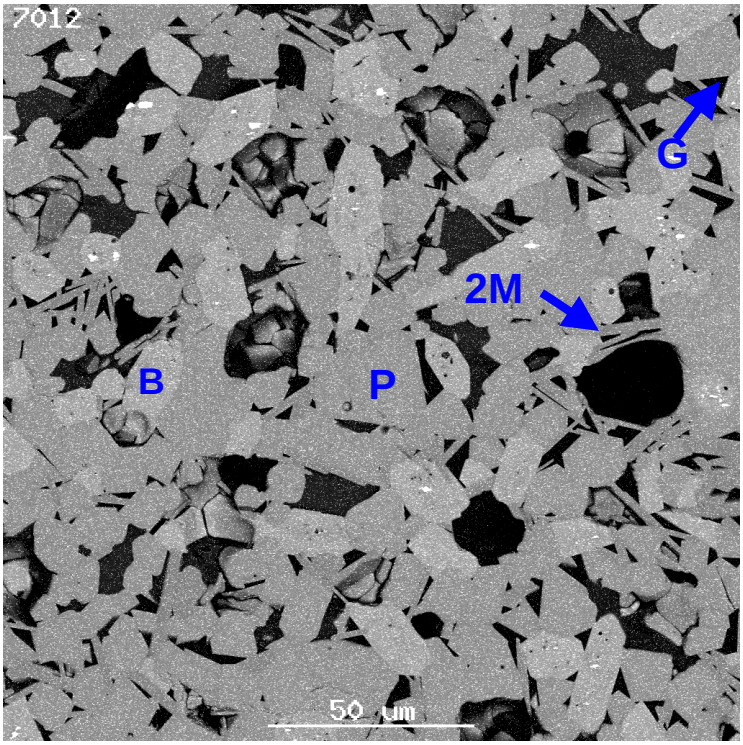
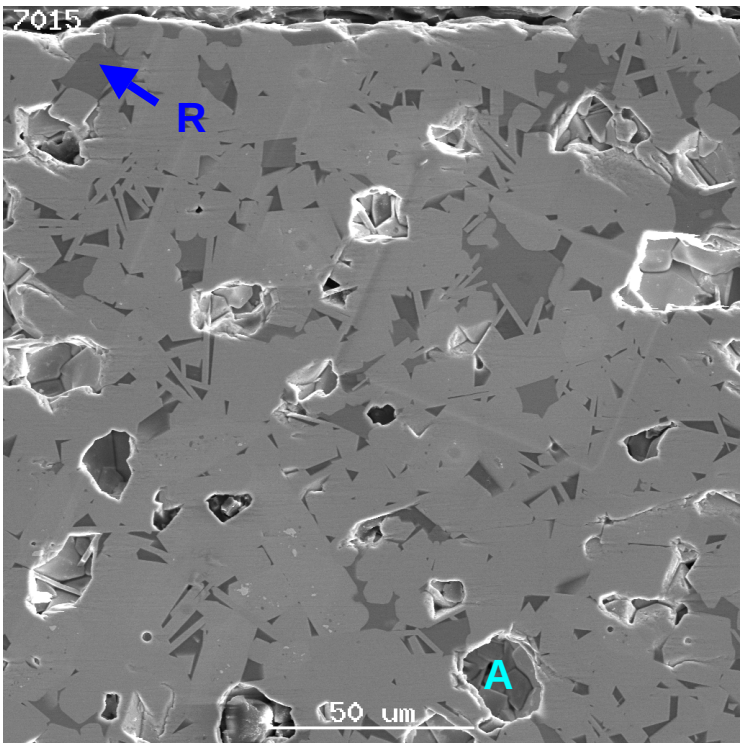


Figure H-6: (a) Secondary electron and (b) backscattered electron micrographs of the middle of pellet Pu11803 (composition B3-13, oxide-route wet-milled, sintered at 1325°C in air for 4 hours). The pellet consists of a pyrochlore (P, matrix), 2M zirconolite (2M, slightly darker and more elongated grains than pyrochlore), Pu/U-brannerite (B, light grey), Hf-doped rutile (R, dark grey), a silicate intergranular phase (G, black), PuO_2 (very small white regions inside some brannerite grains) and porosity (A).

(a)



(b)

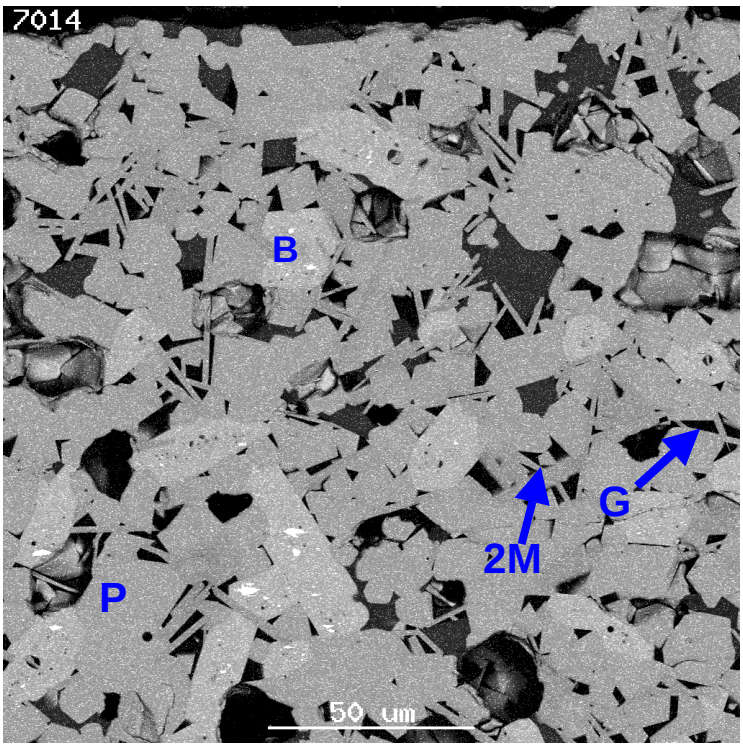


Figure H-7: (a) Secondary electron and (b) backscattered electron micrographs of the top of pellet Pu11803 (composition B3-13, oxide-route wet-milled, sintered at 1325°C in air for 4 hours). The pellet consists of a pyrochlore (P, matrix), 2M zirconolite (2M, slightly darker and more elongated grains than pyrochlore), Pu/U-brannerite (B, light grey), Hf-doped rutile (R, dark grey), a silicate intergranular phase (G, black), PuO_2 (very small white regions inside some brannerite grains) and porosity (A).

H.2 EDS Analyses

Table H-1: EDS analyses of phases (number of cations, except for the silicate phase, which is given in wt. % of element) in the pellets made from Pu/U-doped Baseline plus impurities batch composition A-7 (Pu75). Powder was prepared via oxide-route with wet ball milling. Pellets were sintered in Ar at 1325°C for 4 hours.

Composition	A-7					
	pyrochlore	2M Zirconolite	brannerite	rutile	Pu/U-oxide	Silicate Glass &
~ abundance (vol. %)	70 - 75	10	10	5 - 7	< 1	1 - 2
Element						Wt. %
oxygen	7	7	6	2	2	
Ca	0.98	0.76	0.10	0.003	0.13	
Gd	0.25	0.17	0.17		0.07	
Hf	0.18	0.67	0.09	0.06	0.03	
U	0.43	0.16	0.50	0.01	0.43	
Pu	0.22	0.08	0.22		0.38	
Ti	1.97	1.86	1.99	0.92	0.05	
Al	0.03	0.17	0.03	0.006		
B						
Cr						
Fe		0.06				
Ga		0.03				
K						
Mg		0.04				
Mo						
Na						
Ni						
P						
Si						
Ta						
W						
Zn						
Total	4.06	4.01	3.10	1.00	1.08	

& Too small to analyse accurately

$ The uranium is taken to be U^{4+} for analysis purposes.

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EDS system

The standard error in the individual measurements is ~ 1 %.

Table H-2 - EDS analyses of phases (number of cations, except for the glass phase which is given in wt. % of element present) found at the top middle and bottom of the pellet Pu118 02 (B3-13, baseline + impurities composition, wet ball milled for 16 hours) that had been sintered in Ar at 1325°C for 4 hours.

	top					middle					bottom				
Phase	**pyrochlore**	**brannerite**	**zirconolite**	**rutile**	**glass**	**pyrochlore**	**brannerite**	**zirconolite**	**rutile**	**glass**	**pyrochlore**	**brannerite**	**zirconolite**	**rutile**	
~ abundance (vol. %)	70-80	7-10	10-15	2-3	1-2	70-80	7-10	10-15	2-3	1-2	70-80	7-10	10-15	2-3	
Element					**(Wt.%)**					**(Wt. %)**					**(W**
oxygen	7	6	7	2	44	7	6	7	2	44	7	6	7	2	
Ca	0.88	0.08	0.71		9	0.88	0.07	0.71		9	0.88	0.07	0.69		
Gd	0.25	0.18	0.18		0.1	0.27	0.15	0.19		0.2	0.26	0.13	0.19		
Hf	0.19	0.07	0.67	0.06	0.2	0.19	0.10	0.67	0.05	0.5	0.18	0.10	0.63	0.06	
Pu	0.23	0.27	0.09			0.24	0.19	0.10		0.3	0.24	0.20	0.09		
U [$]	0.43	0.50	0.16	0.009	0.05	0.43	0.53	0.16	0.006	0.1	0.43	0.54	0.16	0.009	
Ti	2.02	1.95	1.89	0.92	3	2.00	2.00	1.88	0.94	3	2.02	1.98	1.91	0.93	
Al		0.05	0.14	0.005	10		0.05	0.14	0.005	10		0.05	0.16	0.005	
B [+]															
Ba					3.5					3.5					
Ce															
Cr															
Cu					0.1					0.1					
Fe			0.04		0.5			0.04	0.002	0.4			0.04	0.002	
Ga			0.06		3			0.06		3.5			0.07		
K					1					1					
La															
Mg					1.5					1					
Mo					0.04					0.05					
Na			0.07	0.002	2			0.08		1.5			0.02		
Nd															
Ni															
P					2					2					
Pb										0.1					
Si					20					20					
Ta															
W															
Zn										0.1					
Total	4.00	3.10	4.01	1.00	100	4.01	3.08	4.02	1.00	100	4.01	3.08	4.01	1.00	

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

* The glass composition is variable across the sample and the analysis is prone to error, values here are given as a guide only.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

The standard error in the individual measurements is ~ 1 %.

Table H-3 - EDS analyses of phases (number of cations, except for the glass phase which is given in wt. % of element present) found at the top middle and bottom of the pellet Pu118 03 (B3-13, baseline + impurities composition, wet ball milled for 16 hours) that had been sintered in air at 1325°C for 4 hours.

	top					middle					bottom				
Phase	**pyrochlore**	**brannerite**	**zirconolite**	**rutile**	**glass**	**pyrochlore**	**brannerite**	**zirconolite**	**rutile**	**glass**	**pyrochlore**	**brannerite**	**zirconolite**	**rutile**	
~ abundance (vol. %)	65-75	10-15	10-15	1-3	1-2	65-75	10-15	10-15	1-3	1-2	65-75	10-15	10-15	1-3	
Element					**(Wt.%)**					**(Wt. %)**					**(W**
oxygen	7	6	7	2	44	7	6	7	2	42	7	6	7	2	
Ca	0.98	0.09	0.73		10	0.99	0.09	0.75		9	0.97	0.10	0.72		
Gd	0.27	0.15	0.20		0.7	0.26	0.18	0.21		0.5	0.27	0.17	0.21		
Hf	0.18	0.11	0.66	0.07	1.3	0.18	0.10	0.65	0.07	0.5	0.19	0.10	0.67	0.07	
Pu	0.25	0.25	0.10			0.24	0.22	0.11			0.25	0.25	0.12		
U [$]	0.41	0.46	0.16	0.01	2	0.42	0.48	0.18	0.01	1.5	0.41	0.45	0.16	0.01	
Ti	1.97	1.98	1.87	0.90	3.5	1.97	1.97	1.85	0.91	3	1.97	1.99	1.87	0.90	
Al		0.06	0.13	0.008	8		0.07	0.12	0.008	8		0.06	0.12	0.01	
B +#															
Ba					3					3					
Ce															
Cr															
Cu					0.5					0.5					
Fe			0.05	0.009	0.5			0.05	0.006	0.5			0.04	0.01	
Ga			0.05		3.5			0.05		3.5			0.05		
K					0.5					0.5					
La															
Mg					2					2					
Mo					0.3					0.3					
Na			0.10		1			0.06		1			0.09		
Nd															
Ni															
P					2					2					
Pb					0.1					1					
Si					19					19					
Ta															
W															
Zn					1					1					
Total	4.06	3.10	4.04	1.00	100	4.06	3.11	4.03	1.00	100	4.05	3.11	4.03	1.01	

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

* The glass composition is variable across the sample and the analysis is prone to error, values here are given as a guide only.

\# B is not detected by the EDS system.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

The standard error in the individual measurements is ~ 1 %.

H.3 XRD Results

Table H-4: A summary of the XRD results for Pu/U/Hf-baseline + impurities samples.

Description - Processing Route			
Route/Milling/Sint. Temp. (°C)/ Sint. atmosphere /Sample No.	**XRD Description**	**XRD File Name.**	**Phases Present**
A-7			
oxide/wet ball/1325/Ar/Pu75	Ground pellet surface	s14880	pyrochlore, 2M zirconolite, brannerite, rutile
B3-13			
oxide/wet ball/1325/Ar/Pu11802	Ground pellet surface	s16307	pyrochlore, 2M zirconolite, brannerite,
oxide/wet ball/1325/air/Pu11803	Ground pellet surface	S16308	pyrochlore, 2M zirconolite, brannerite, possibly rutile

The above Table contains a list of the raw XRD data files taken using a Siemens D500 Diffractometer (Co K-alpha). The patterns are from polished surfaces of pellets. The broad low angle peak ~ 15 - 25° (2 theta) in some of the patterns is from the resin used to mount the samples. The raw data files are on the enclosed computer disk.

s*.raw files are Siemens D500 files.

H.3.1 A-7 Oxide-route Wet Ball Milled Sample Fired at 1350°C in Ar

The XRD pattern consists of pyrochlore, 2M zirconolite, brannerite and rutile. This is consistent with the SEM analysis.

H.3.2 B3-13 Oxide-route Wet Ball Milled Sample Fired at 1350°C in Ar

The XRD pattern consists of pyrochlore, brannerite and rutile. This is consistent with the SEM analysis.

H.3.3 B3-13 Oxide-route Wet Ball Milled Sample Fired at 1350°C in Air

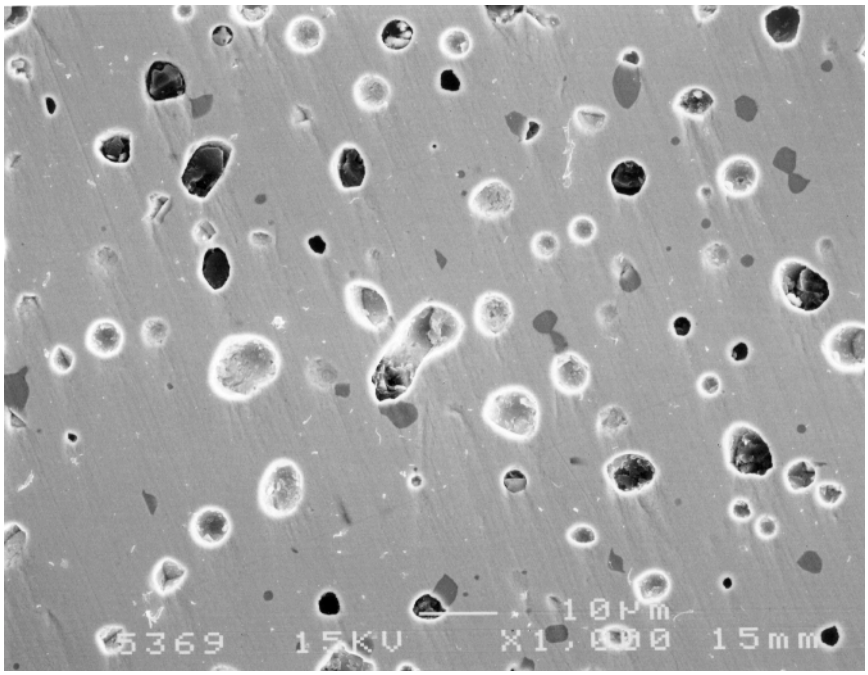
The XRD pattern consists of pyrochlore, brannerite and rutile. This is consistent with the SEM analysis. The brannerite peaks are slightly more intens than those in the Ar sintered sample.

APPENDIX I

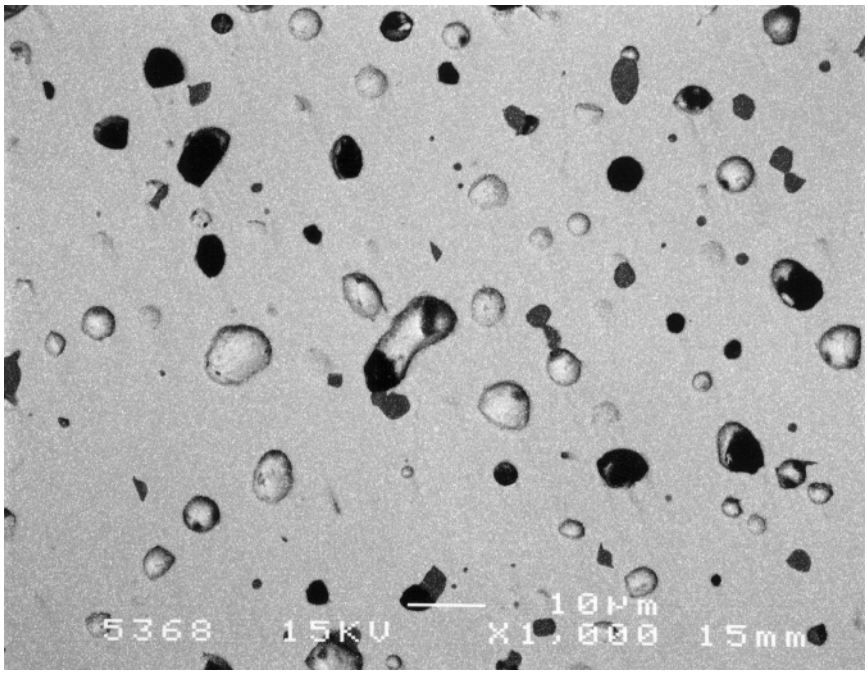
SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-13 - Pu/U-DOPED “NOMINALLY” 10 % PEROVSKITE CERAMIC

I. APPENDIX I: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES OF COMPOSITION B1-13 - PU/U-DOPED “NOMINALLY” 10 % PEROVSKITE CERAMIC

I.1 SEM IMAGES



(a)



(b)

Figure I-1: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws980361 (Pu105-01A) (composition B1-13, “nominally” ~ 10 % perovskite, alkoxide-route, wet-milled 16 hours, sintered at 1350°C in Ar for 4 hours). The matrix is pyrochlore; the dark-grey phase is rutile. Porosity (see (a)) is also present. No perovskite or brannerite was detected in this sample.

I.2 EDS ANALYSES

Table I-1: EDS analyses of phases (number of cations) in the pellets made of composition B1-13, Pu/U-doped, wet-milled oxide-route batch. Pellets were sintered in Ar at 1350°C for 4 hours.

Sample No.	**Pu101-01a (mws980356)**	
Route	**oxide**	
	pyrochlore	**rutile**
~ abundance (vol. %)	95	5
Element		
oxygen	7	2
Ca	1.03	0.004
Gd	0.20	
Hf	0.22	0.06
U	0.35	0.004
Pu	0.23	0.001
Ti	2.04	0.94
Total	4.07	1.00

$ The uranium is taken to be U^{4+} for analysis purposes.

Note: the absence of a value for an element means that the element is either absent or is present in amounts below the detection limits of the EI system

The standard error in the individual measurements is ~ 1 %.

I.3 XRD RESULTS

Table I-2: A summary of the XRD results for samples made of composition B1-13 (Pu/U/Hf – "nominally" 10 % perovskite ceramic).

Description - Processing Route			
Route/Milling/Sint. Temp. (^{o}C)/ Sint. atmosphere /Sample No.	**XRD Description**	**XRD File Name.**	**Phases Present**
oxide/wet ball/1350/Ar/ Pu10501	Ground pellet surface	s15054, t1339	pyrochlore, rutile

The above Table contains a list of the raw XRD data files. Note that those starting with t are Scintag Diffractometer files (Cu K-alpha radiation) and those starting with S are Siemens D500 Diffractometer data files (Co K-alpha). The broad low angle peak ~ 15 - 25° (2 theta) in some of the patterns is from the resin used to mount the samples. The raw data files are on the enclosed computer disk.

s*.raw files are Siemens D500 files

t*.raw files are Scintag raw files using DMSNT Version 1.3 (Diffraction Management System) for Microsoft Windows NT 4.0, t*.txt are text files of Scintag files, t*.rd are Scintag files exported as older version Scintag binary files.

I.3.1 Alkoxide-route Wet Ball Milled Sample Fired at 1350^{o}C in Ar

The XRD pattern consists of pyrochlore and rutile. This is consistent with the SEM analysis.