$CaUTi_2O_7$ ceramics for actinide disposition

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Background

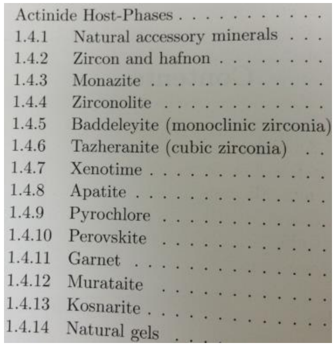
Nuclear industry

High-level waste (HLW)

89 Ac	90 Th	91 Pa	92 U	93 Np
94 Pu	95 Am	96 Cm	97 Bk	98 Cf
99 Es	100 Fm	101 Md	102 No	103 Lr

Actinide

Immobilisation
Ceramics


Actinide Host-Phases
1.4.1 Natural accessory minerals
1.4.2 Zircon and hafnon
1.4.3 Monazite
1.4.4 Zirconolite
1.4.5 Baddeleyite (monoclinic zirconia)
1.4.6 Tazheranite (cubic zirconia)
1.4.7 Xenotime
1.4.8 Apatite
1.4.9 Pyrochlore
1.4.10 Perovskite
1.4.11 Garnet
1.4.12 Murataite
1.4.13 Kosnarite
1.4.14 Natural gels

Ceramic matrices

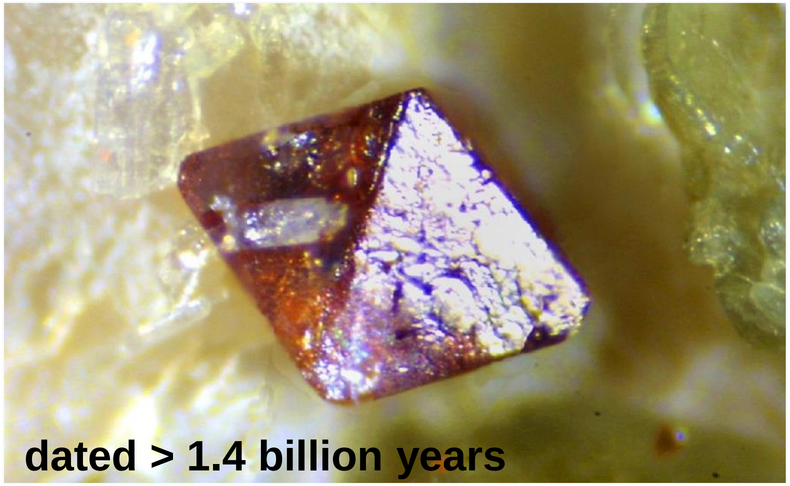
Depleted, Natural and Low-Enriched Uranium (DNLEU)

160,000 – 180,000 tU stock in UK (tonnes of uranium) over the period 2007-2013.

Crystal chemical design strategy

Minerals: Nature's wasteforms
Retains actinides over geological timescales

Pyrochlore: $(Y,Na,Ca,U)_2(Nb,Ta,Ti)_2O_7$



Parent formula: $A_2B_2O_7$

Coordination Number = 8 6

Stable under environmental conditions[1,2]

Wasteform formulation

Betafite: $CaUTi_2O_7$

- U_3O_8 adding into $CaTiO_3$-TiO_2-ZrO_2 precursors;
- Fe and Ni buffer to control oxidation state and phase present.

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1. Am. Miner. 81, 1237 (1996)
2. Radiochim. Acta 88, 539 (2000)

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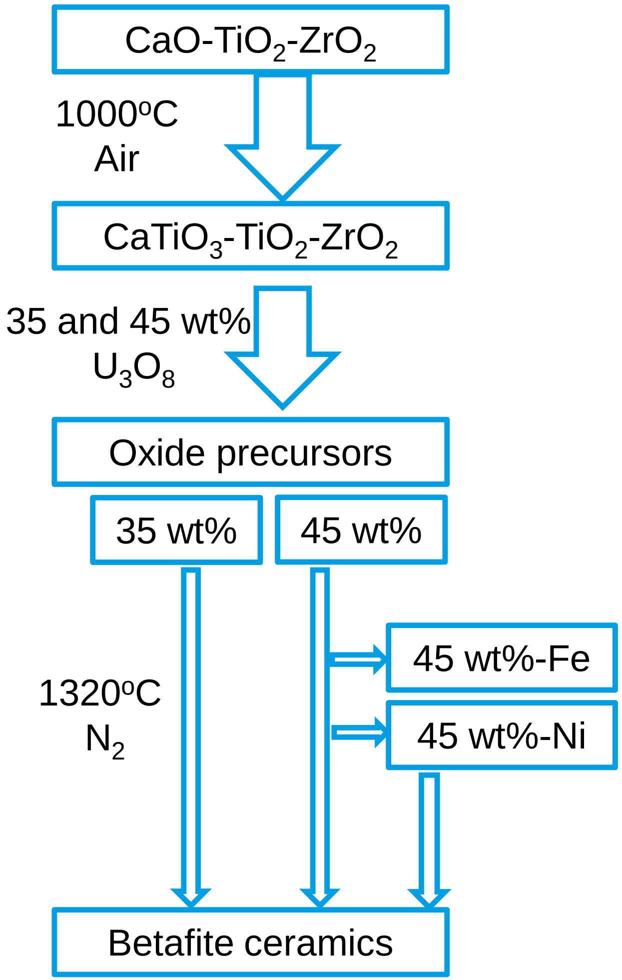
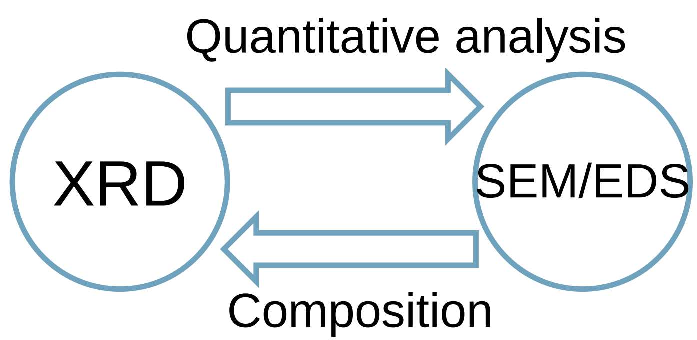
Experimental

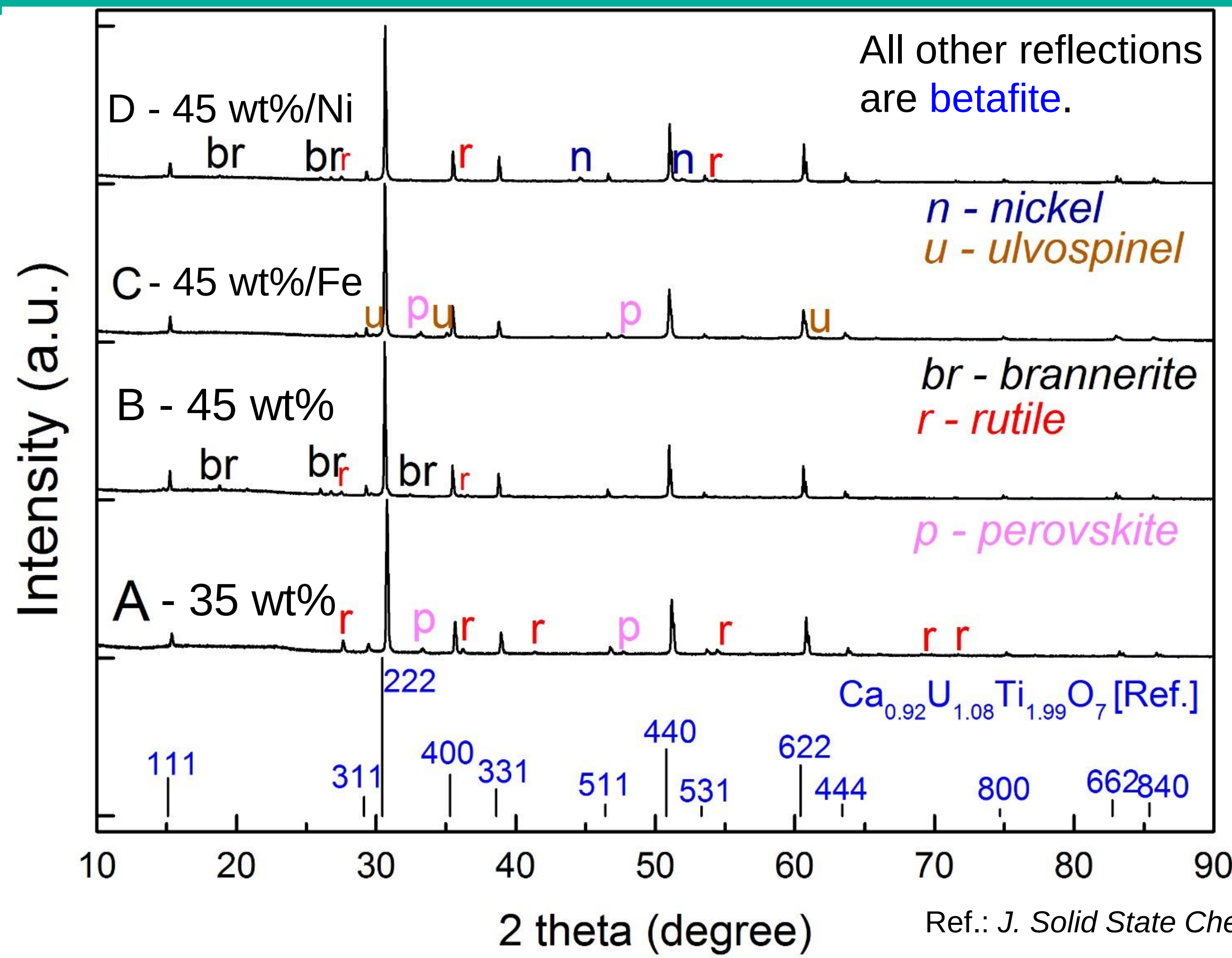


Label	Nominal	U_3O_8/Buffer Loading (wt%)
A	$Ca_{0.96}U_{0.482}Zr_{0.177}Ti_{2.203}O_7$	35/-
B	$Ca_{0.872}U_{0.669}Zr_{0.161}Ti_{2.01}O_7$	45/-
C	$Ca_{0.872}U_{0.669}Zr_{0.161}Ti_{2.01}O_7$-Fe	40.5/10
D	$Ca_{0.872}U_{0.669}Zr_{0.161}Ti_{2.01}O_7$-Ni	40.5/10

- ✓ Phase assemblage
- ✓ Chemical composition
- ✓ Quantitative phase analysis (QPA)
- ✓ Oxidation state of U



Results and discussion



UTi_2O_6
TiO_2
Ni

Fe_2TiO_4
$CaTiO_3$

TiO_2
UTi_2O_6

TiO_2
$CaTiO_3$

Ref.: *J. Solid State Chem.*, 82,146 (1989)

- ✓ Nearly single-phase with some minor phases;
- ✓ No free uranium oxide.

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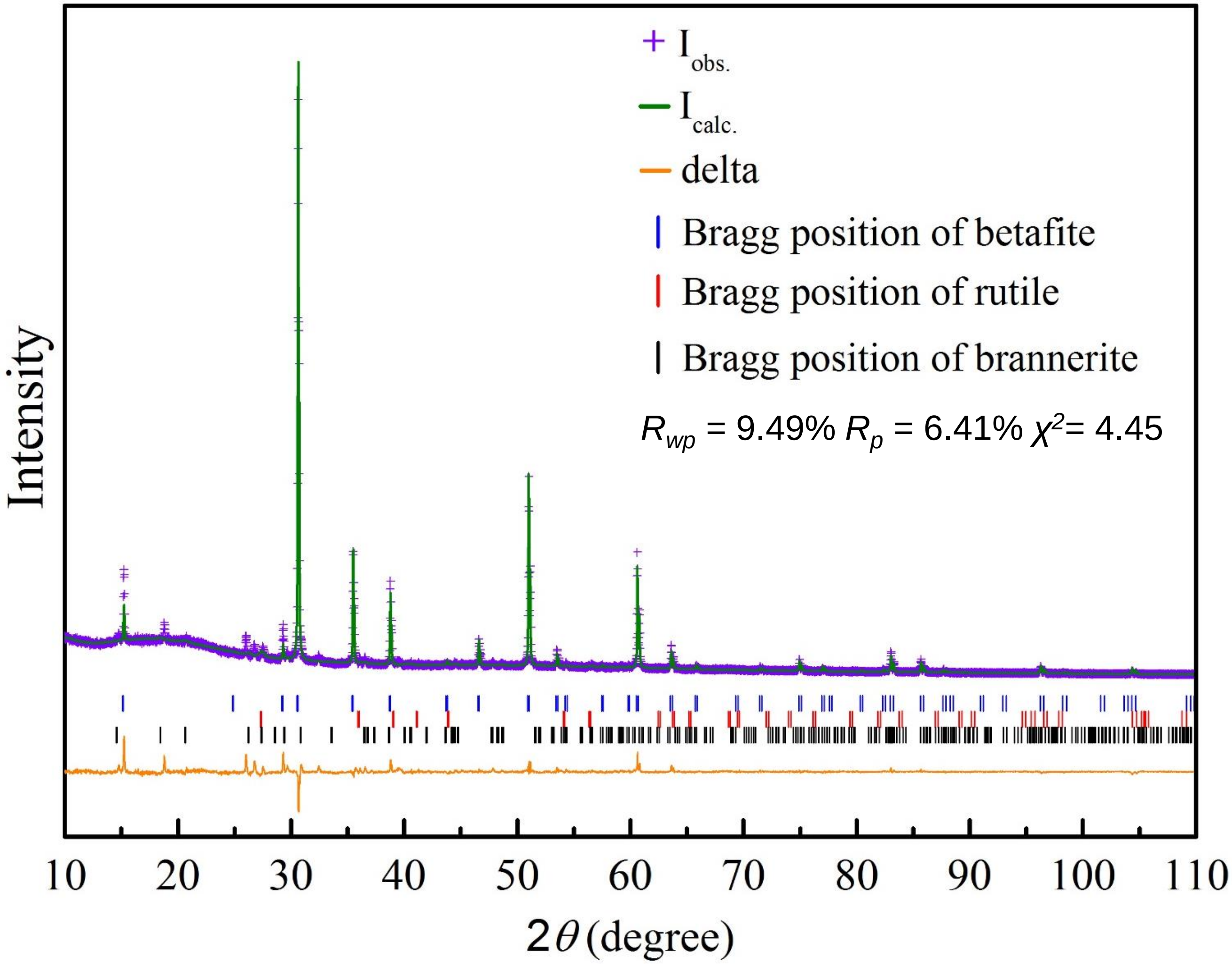
QPA using Rietveld refinement



Rietveld refinement of the XRD pattern for the as-sintered sample B.

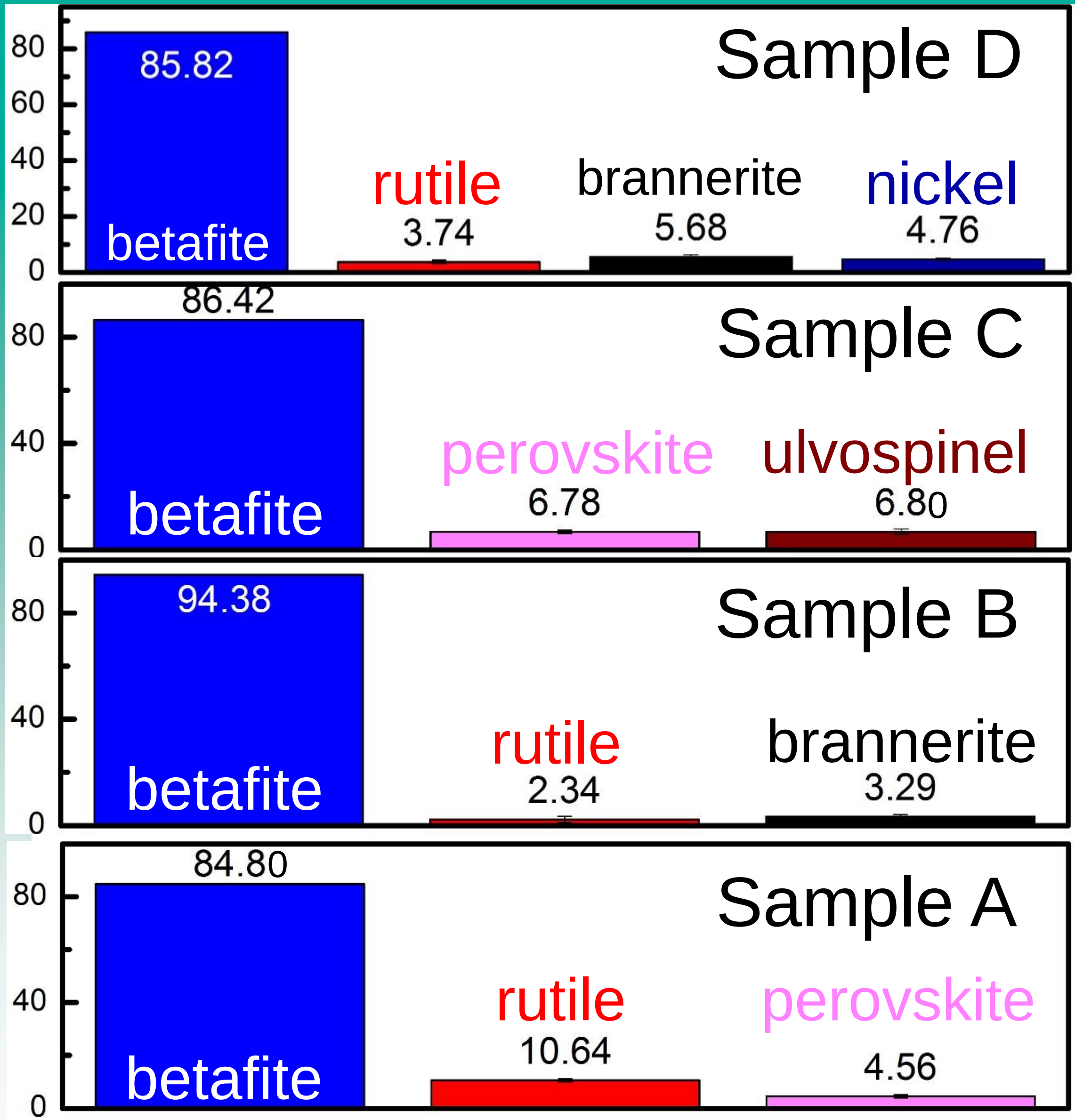
$$w_i = \frac{S_i M_i V_i}{\sum_j S_j M_j V_j}$$

wi: weight fraction

Si: refined scale factor

Mi and *Vi* are the unit cell mass and volume

Quantitative phase analysis



Phase	*Amount (wt%)*
Betafite	85.82 ± 0.11
Ni	4.76 ± 0.46
Brannerite	5.68 ± 0.68
Rutile	3.74 ± 0.63
Betafite	86.42 ±0.11
Perovskite	6.78 ± 0.66
Ulvospinel	6.80 ± 1.02
Betafite	94.38 ± 0.07
Rutile	2.34 ± 1.20
Brannerite	3.29 ± 0.86
Betafite	84.80% ± 0.24
Rutile	10.64 ± 0.65
Perovskite	4.56 ± 0.59

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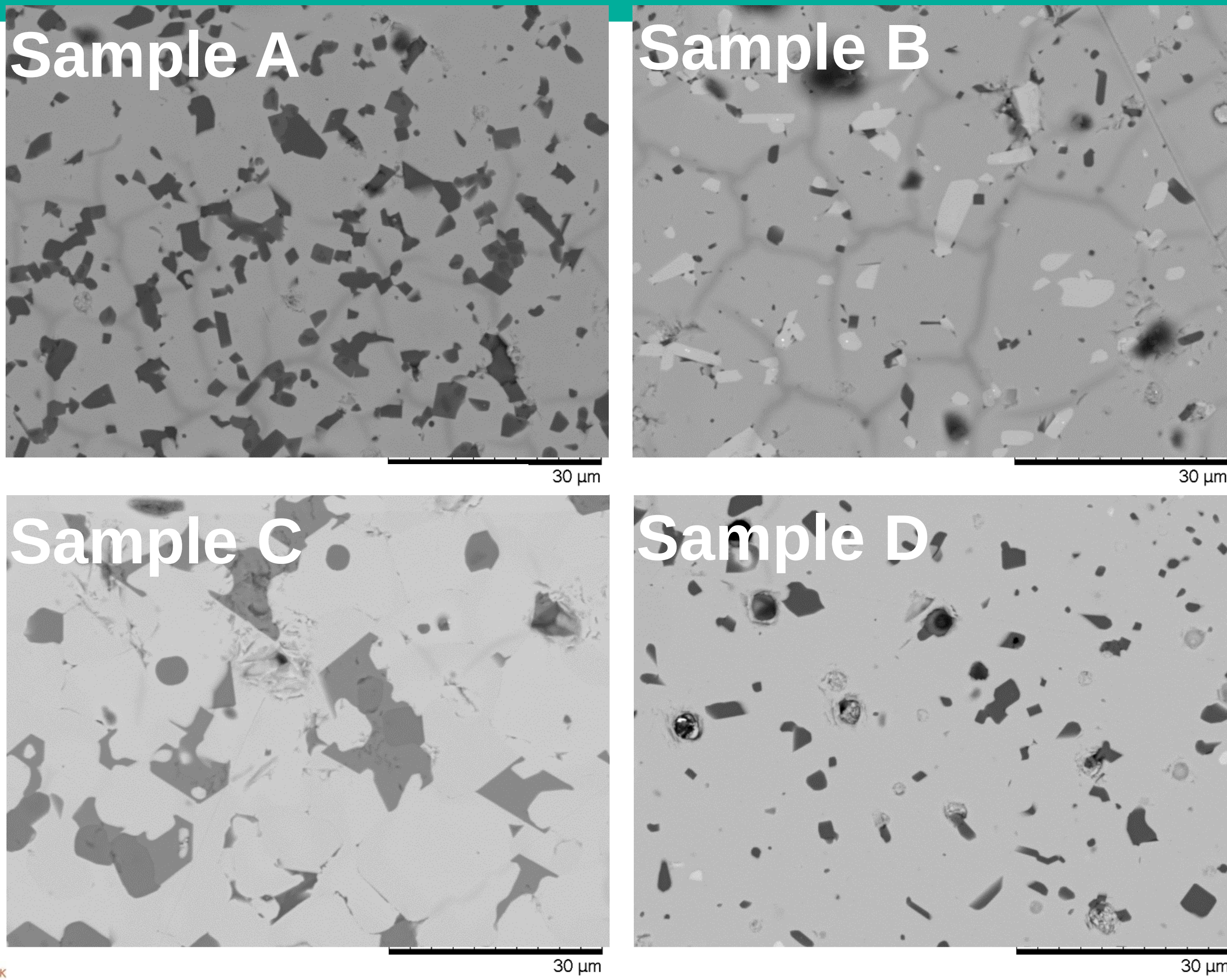
SEM observation



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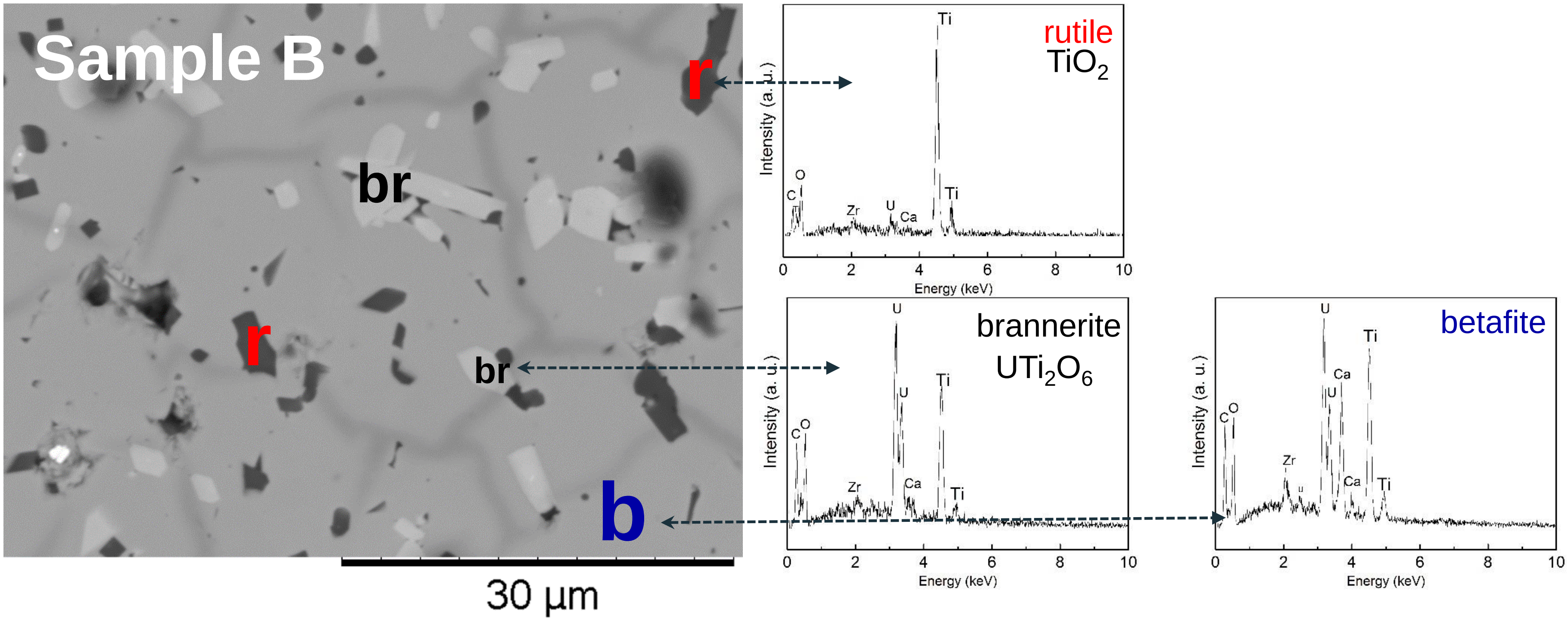
Chemical composition



Composition of betafite phase by EDS

A	$Ca_{1.13(5)}U_{0.55(4)}Zr_{0.17(2)}Ti_{2.15(8)}O_7$
B	$Ca_{1.09(4)}U_{0.67(4)}Zr_{0.15(3)}Ti_{2.10(7)}O_7$
C	$Ca_{0.90(5)}U_{0.71(5)}Zr_{0.15(2)}Ti_{1.97(6)}Fe_{0.28(6)}O_7$
D	$Ca_{1.03(2)}U_{0.64(3)}Zr_{0.14(2)}Ti_{2.17(5)}O_7$

Nominal composition

A	$Ca_{0.96}U_{0.482}Zr_{0.177}Ti_{2.203}O_7$
B	$Ca_{0.872}U_{0.669}Zr_{0.161}Ti_{2.01}O_7$

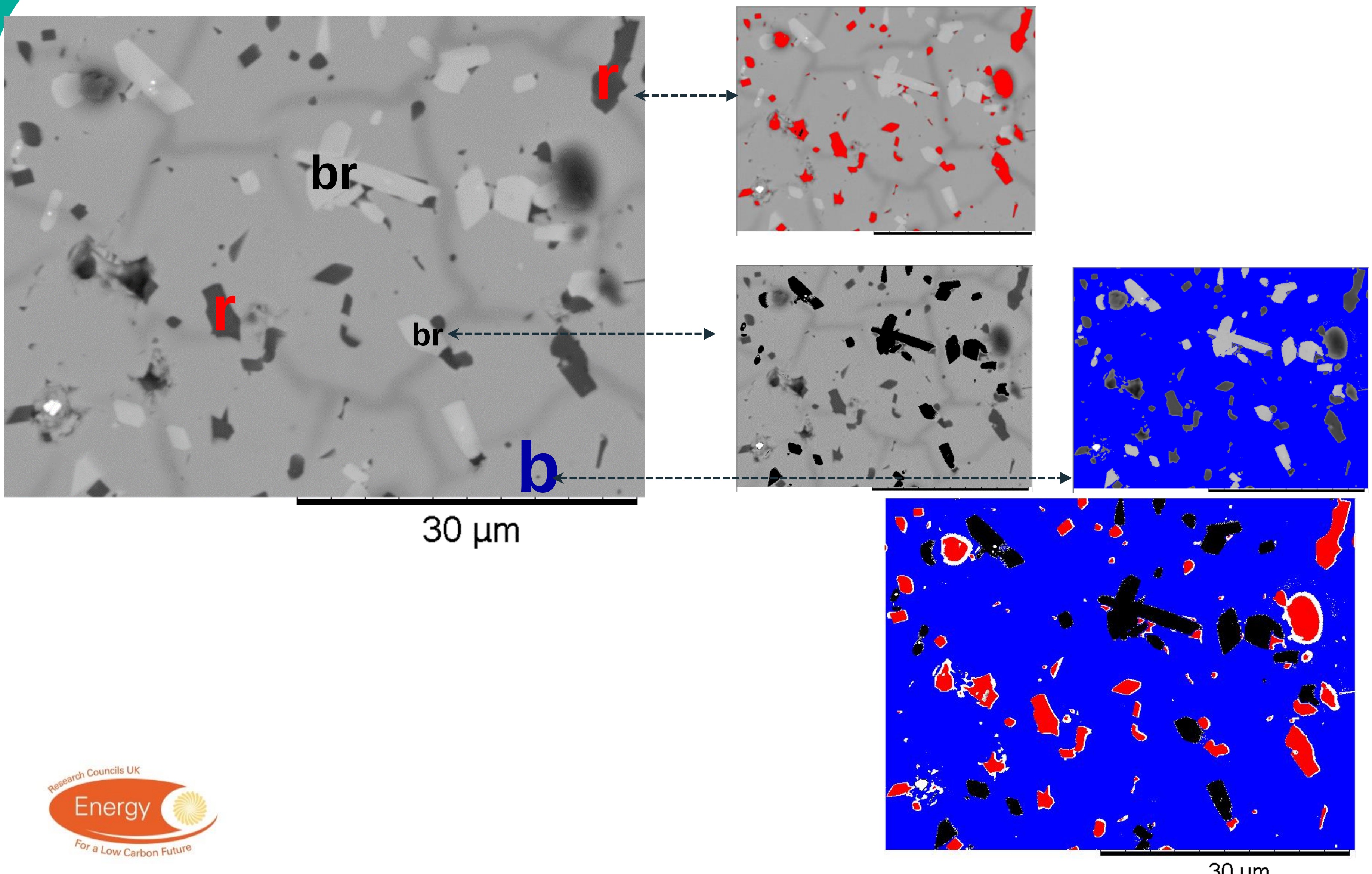
Ref.

single-phase $Ca_{1.25}U_{0.75}Ti_2O_7$

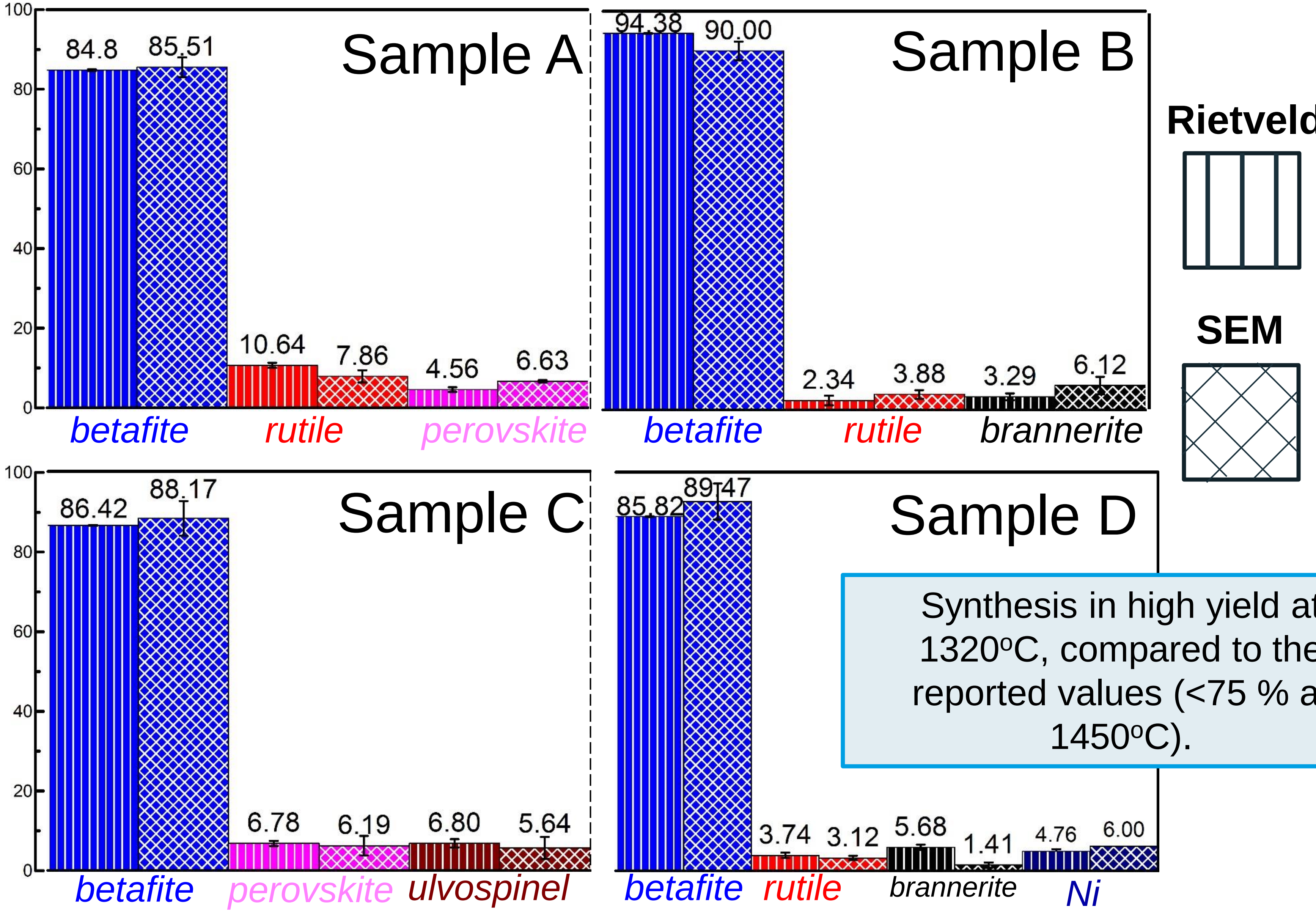
single-phase $Ca_{1.4}U_{0.7}Ti_{1.9}O_7$

Ref. *J. Am. Ceram. Soc.*, 93 3464 (2010)

QPA using image analyses



Comparison



Synthesis in high yield at 1320ºC, compared to the reported values (<75 % at 1450ºC).

Checking calculation

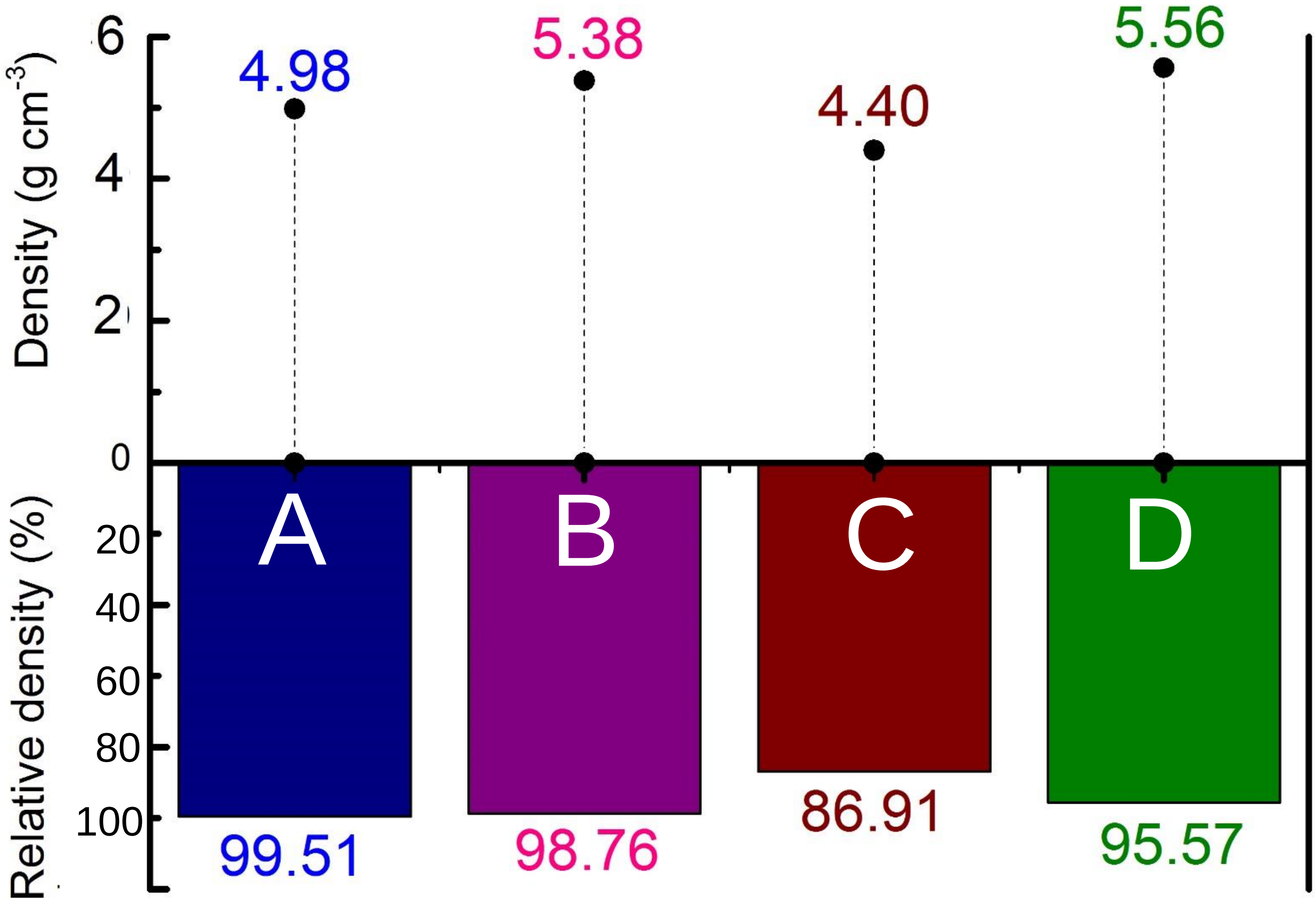
The contents of the starting oxides were checked and compared.

B	Raw materials	Rietveld	SEM
CaO	11.73	13.33 ± 0.03	12.94 ± 0.38
TiO_2	38.50	40.00 ± 1.56	41.50 ± 2.88
ZrO_2	4.77	4.01 ± 0.00	3.87 ± 0.10
U_3O_8	45.00	42.66 ± 0.52	42.92 ± 2.30

Close!

Sample B	Raw materials	Rietveld	SEM
CaO	11.73	13.33 ± 0.03	12.94 ± 0.38
TiO_2	38.50	40.00 ± 1.56	41.50 ± 2.88
ZrO_2	4.77	4.01 ± 0.00	3.87 ± 0.10
U_3O_8	45.00	42.66 ± 0.52	42.92 ± 2.30

Densification



Near fully-densification.

Note: theoretical density is calculated by Rietveld method.

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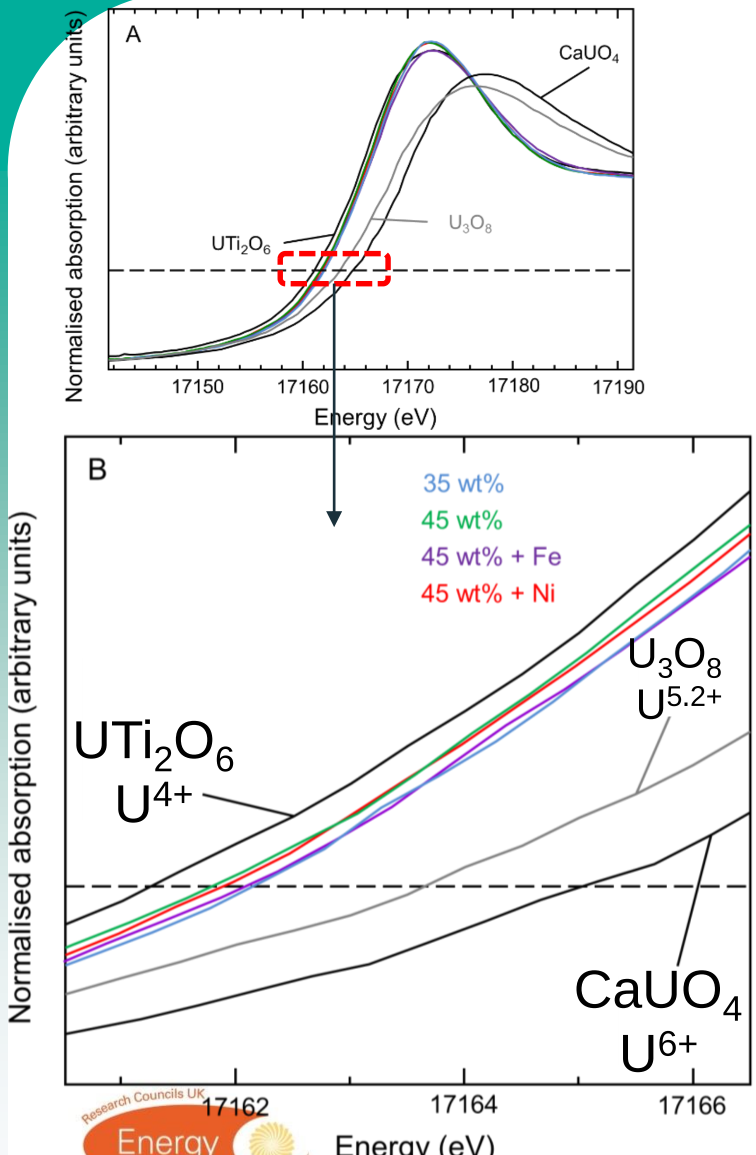
Oxidation state of U



Sample	Average oxidation state (v.u) $\pm$ 0.1	% U^{6+} $\pm$ 5
U_3O_8	5.2	60
A	4.3	15
B	4.4	20
C	4.5	25
D	4.5	25

All 4 samples showed an average oxidation state of 4.4 $\pm$ 0.1.

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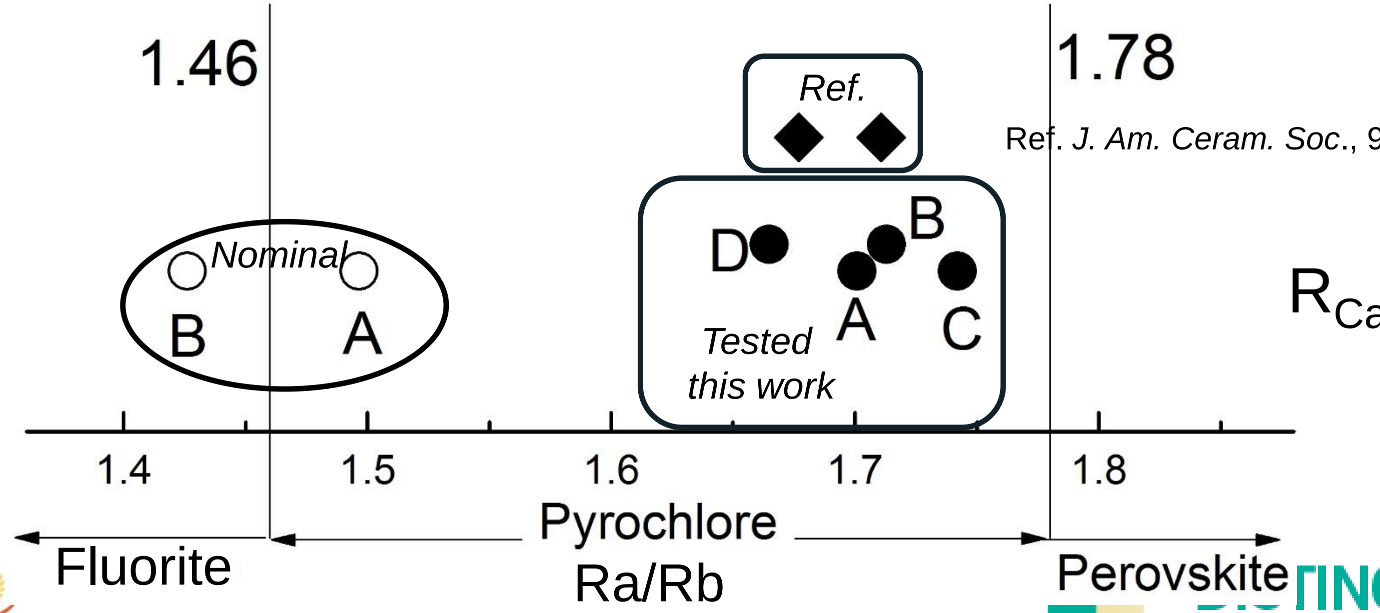
Radius ratio

Chemical composition in Betafite phase

Sample A	$Ca_{1.13}U^{4+}_{0.47}U^{6+}_{0.08}Zr_{0.17}Ti_{2.15}O_7$
Sample B	$Ca_{1.09}U^{4+}_{0.54}U^{6+}_{0.13}Zr_{0.15}Ti_{2.10}O_7$
Sample C	$Ca_{0.90}U^{4+}_{0.53}U^{6+}_{0.18}Zr_{0.15}Ti_{1.97}Fe_{0.28}O_7$
Sample D	$Ca_{1.03}U^{4+}_{0.48}U^{6+}_{0.16}Zr_{0.14}Ti_{2.17}O_7$



Ref. *J. Am. Ceram. Soc.*, 93 3464 (2010)

Conclusion

- ✓ Nearly-pure betafite pyrochlore ceramics with the high relative density were prepared in this work.

- ✓ We demonstrated the synthesis of betafite pyrochlores in high yield at relatively low temperature (>85% at 1320^{o}C) compared to previous studies (<75% at 1450^{o}C).

- ✓ Starting from the nominal composition with the deficient Ca, the content of Ca increased in the betafite phase, resulting in a higher radius ratio favoured by pyrochlore structure.

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Future work

- ✓ Phase diagram study, e.g. increase Ca content.
- ✓ Stability study using ion beam.

Thanks for your attention!