# Ceramic and glass-ceramic wasteforms for actinide disposition

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DISTINCTIVE - 2nd Annual Meeting
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# Actinide Host-Phases

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

- ~ 5 tPu unsuitable for reuse
- ~ 180,000 tU UK-owned DNLEU

Immobilisation

## Wasteform:

- ❑ Ceramic
- ❑ Glass-ceramic

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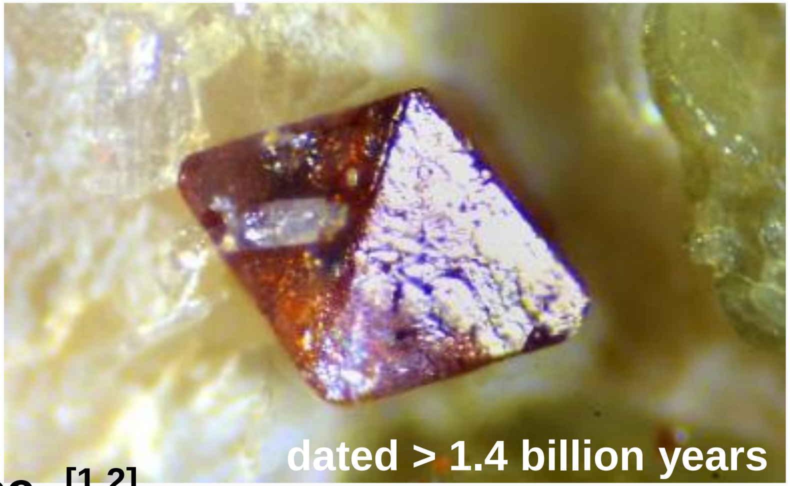
# Pyrochlore ceramics

**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

**Chemical durability and radiation tolerance.** [1,2]

**Wasteform formulation**

Ce-pyrochlore: $CaCeTi_2O_7$

Ce: Surrogate for Pu
$Ce^{4+}$ (0.97 Å, CN = 8) vs.
$Pu^{4+}$ (0.96 Å, CN = 8)

U-Betafite: $CaUTi_2O_7$

Pyrochlore
$U_3O_8$ loading (35 wt% and 45 wt%)
Metallic addition


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

# Experimental - Cerium pyrochlore

$$CaCO_3\text{-}TiO_2\text{-}CeO_2 \xrightarrow[\text{intermediate grinding every 10 hrs}]{1250^{o}C/30h,\ Air} \text{Ce-pyrochlore}$$

Targeting the single phase of cerium pyrochlore

- ✓ Phase assemblage (XRD/QPA)
- ✓ Chemical composition (EDS/XRF)
- ✓ Crystal structure (ND)
- ✓ Oxidation state of Ce (XANES)

XRD: X-ray diffraction
QPA: Quantitative phase analysis
EDS: Energy-dispersive X-ray spectroscopy
XRF: X-ray fluorescence
ND: Neutron diffraction
XANES: X-ray absorption near edge structure

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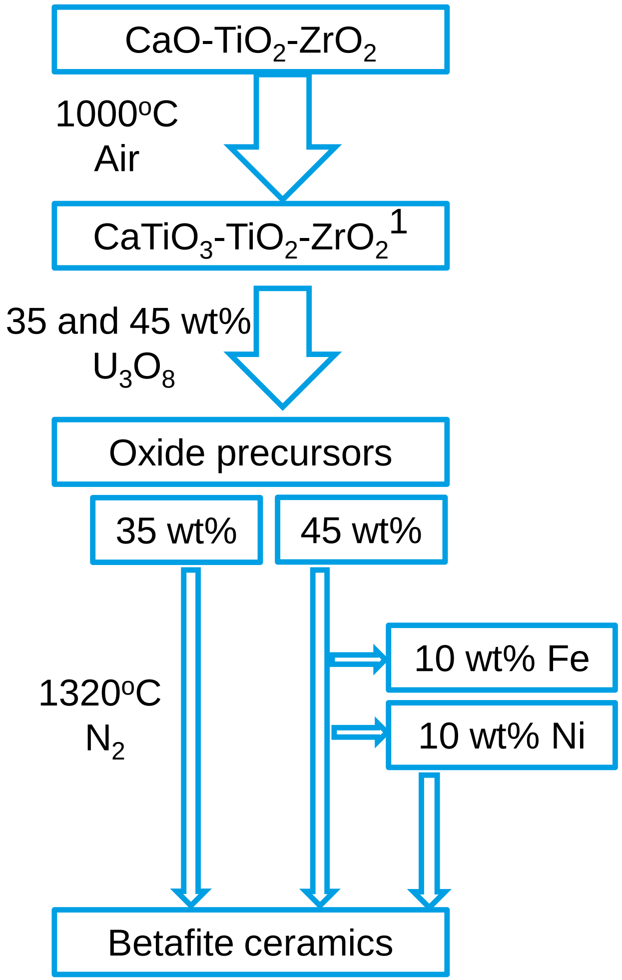
# Experimental - Uranium betafite



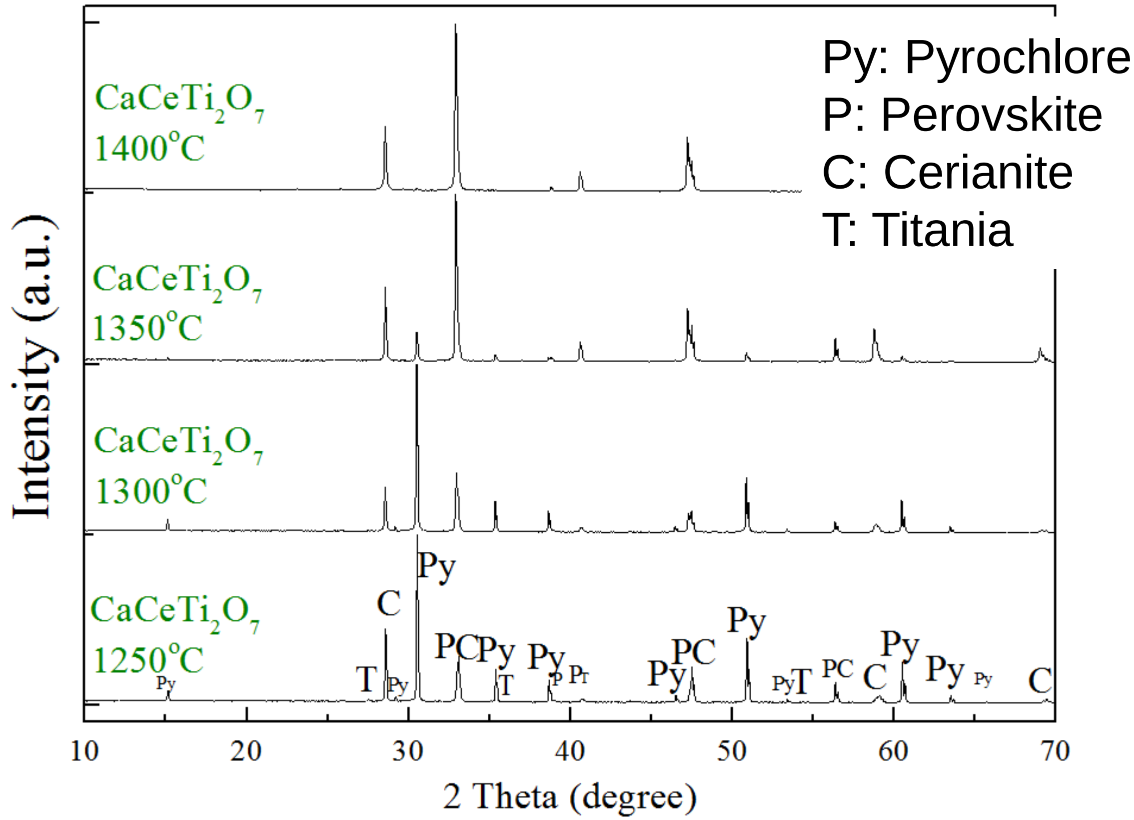

| Label | Nominal | $U_3O_8$/Buffer Loading (wt%) |
|---|---|---|
| **U35** | $Ca_{0.96}U_{0.482}Zr_{0.177}Ti_{2.203}O_7$ | 35/- |
| **U45** | $Ca_{0.872}U_{0.669}Zr_{0.161}Ti_{2.01}O_7$ | 45/- |
| **U45Fe** | $Ca_{0.872}U_{0.669}Zr_{0.161}Ti_{2.01}O_7$-Fe | 40.5/10 |
| **U45Ni** | $Ca_{0.872}U_{0.669}Zr_{0.161}Ti_{2.01}O_7$-Ni | 40.5/10 |

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

1. Provided by NNL

# Ce-pyrochlore: Phase assemblage

$CaCeTi_2O_7$ product starting from the stoichiometric ratio




Ce-pyrochlore

Impurity:

Perovskite, $CeO_2$

$CaCeTi_2O_7$ pyrochlore was stabilised for Ca deficient stoichiometry [Ref. 1]

A careful study of pyrochlore systhesis was performed involving Ca deficiency with an excess of Ti.

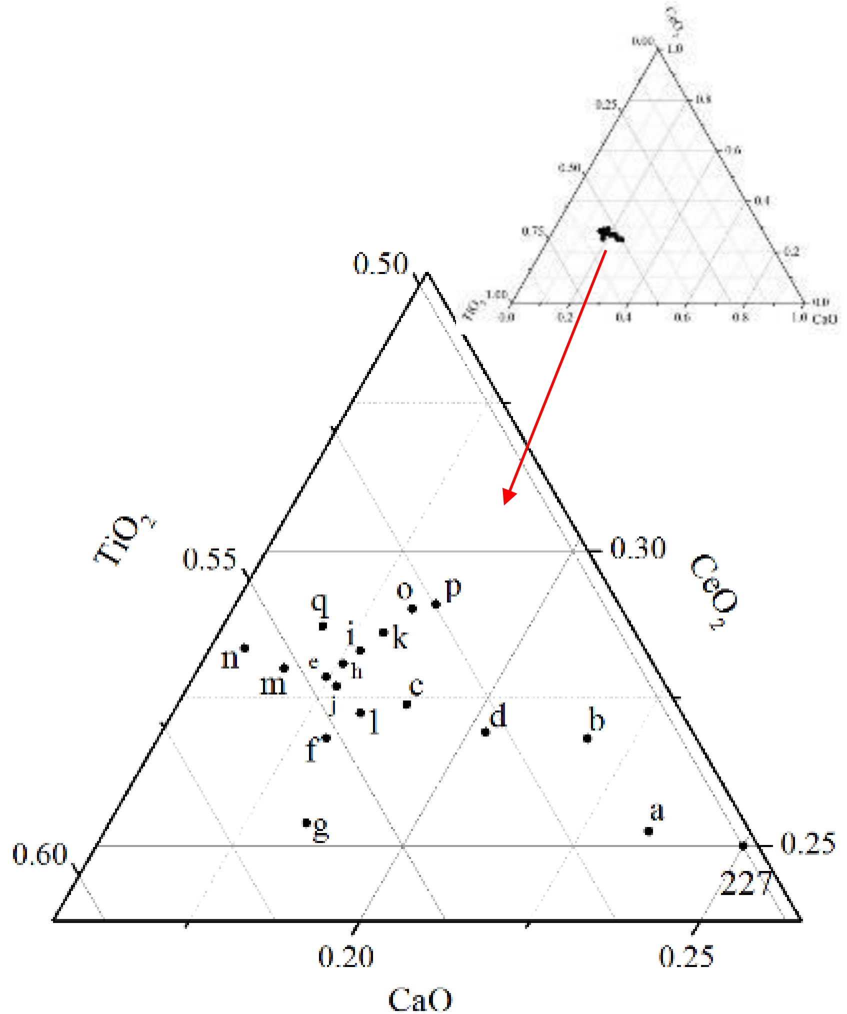

1.*J. Nucl. Mater.*, 303 (2002) pp. 226.

# Ce-pyrochlore: Starting composition

| Composition | Labels |
|---|---|
| Ca1.00Ce1.00Ti2O7 | 227 |
| Ca0.93Ce1.00Ti2.04O7 | a |
| Ca0.86Ce1.05Ti2.02O7 | b |
| Ca0.73Ce1.06Ti2.08O7 | c |
| Ca0.79Ce1.05Ti2.06O7 | d |
| Ca0.67Ce1.07Ti2.10O7 | e |
| Ca0.69Ce1.03Ti2.12O7 | f |
| Ca0.71Ce0.98Ti2.17O7 | g |
| Ca0.67Ce1.07Ti2.07O7 | h |
| Ca0.68Ce1.09Ti2.07O7 | i |
| Ca0.68Ce1.06Ti2.10O7 | j |
| Ca0.69Ce1.10Ti2.06O7 | k |
| Ca0.70Ce1.05Ti2.10O7 | l |
| Ca0.64Ce1.07Ti2.11O7 | m |
| Ca0.61Ce1.08Ti2.12O7 | n |
| Ca0.70Ce1.12Ti2.04O7 | o |
| Ca0.71Ce1.12Ti2.02O7 | p |
| Ca0.65Ce1.10Ti2.08O7 | q |

Deficient Ca

Excess Ti




$CaO-CeO_2-TiO_2$ ternary phase diagram

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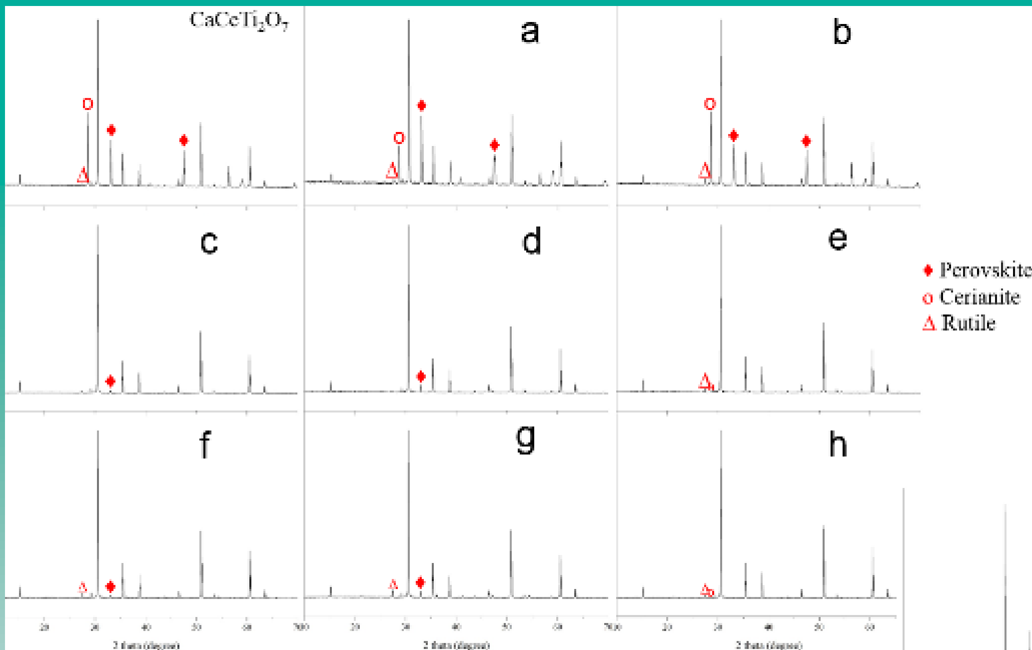
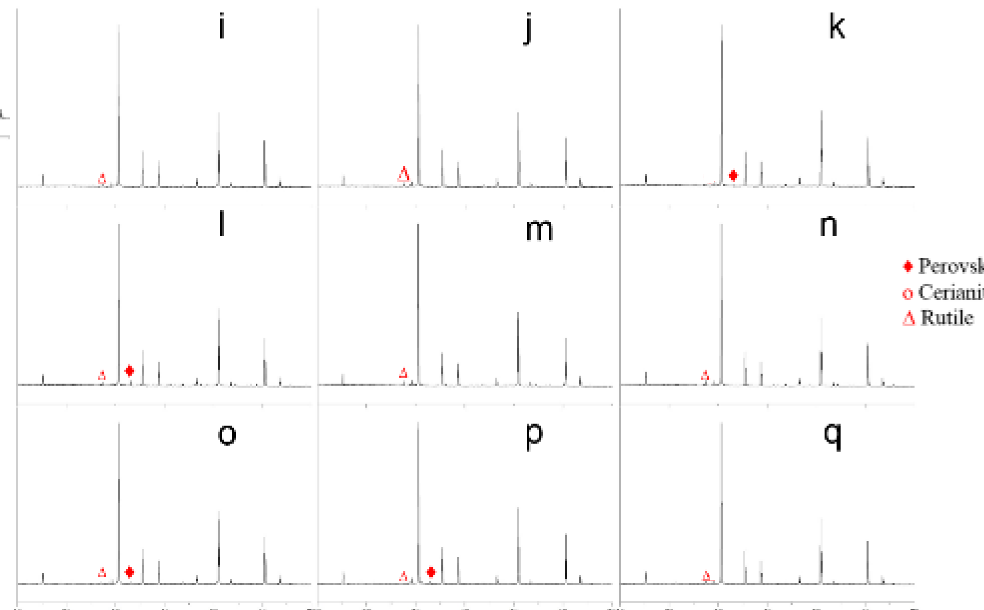
# Ce-pyrochlore: Phase assemblage




The intensity of the impurity peaks decreased.

A nearly single phase was prepared.




♦ Perovskite
o Cerianite
Δ Rutile

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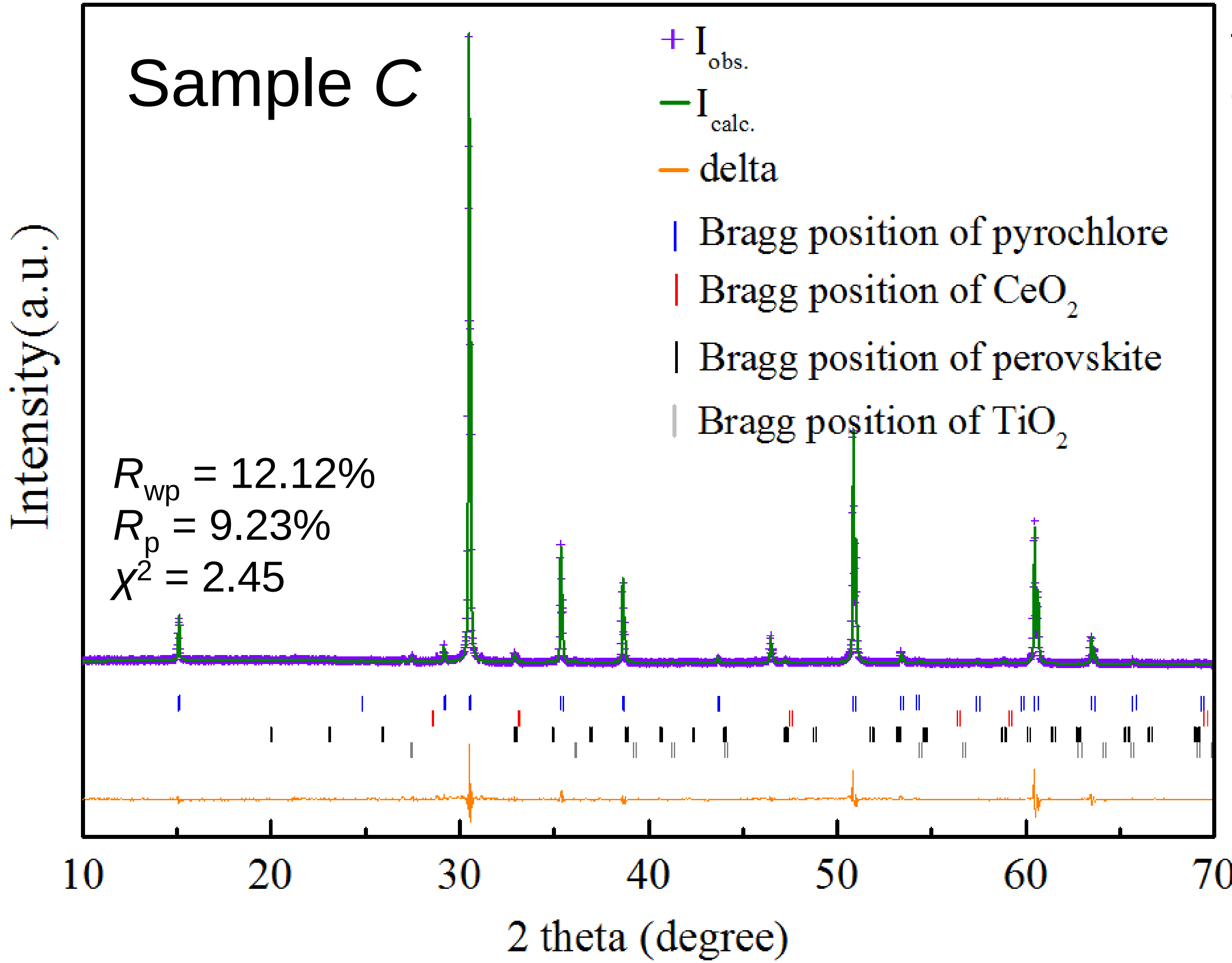
# Ce-pyrochlore: Rietveld quantitation refinement




The weight fraction, $W_i$, can be calculated

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

S: scale factor
M: unit cell mass
V: unit cell volume

| | |
|---|---|
| Pyrochlore | 96.11 wt% |
| $CeO_2$ | - |
| Perovskite | 2.61 wt% |
| $TiO_2$ | 1.27 wt% |

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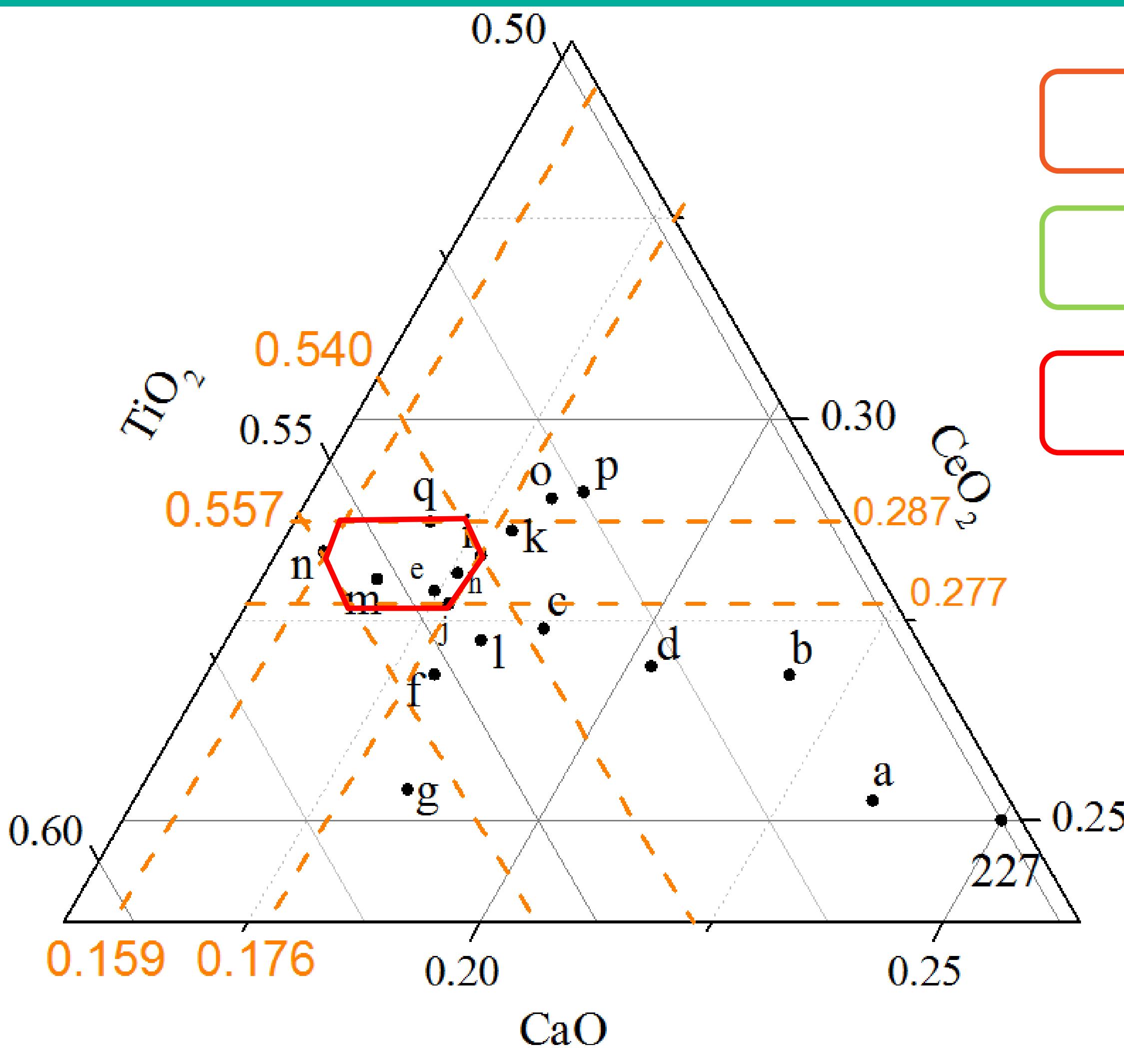
# Ce-pyrochlore: Pyrochlore content

| Labels | Pyrochlore | Impurity | Labels | Pyrochlore | Impurity |
|---|---|---|---|---|---|
| 227 | 58.04% | P, C, T | *i* | 98.09% | T |
| *a* | 51.68% | P, C, T | *j* | 97.26% | P, T |
| *b* | 62.02% | P, C, T | *k* | 99.02% | P, T |
| *c* | 96.11% | P, T | *l* | 91.21% | P, T |
| *d* | 93.78% | P, T | *m* | 95.41% | T |
| *e* | 96.42% | P, T | ***n*** | **94.38%** | **T** |
| *f* | 93.30% | P, T | *o* | 97.70% | P |
| *g* | 86.98% | P, T | *p* | 96.69% | P, C |
| *h* | 96.04% | T | *q* | 96.97% | T |
| P: Perovskite; C: $CeO_2$; T: $TiO_2$. | | | | | |

Sample *n* ($Ca_{0.61}Ce_{1.08}Ti_{2.12}O_7$) with only $TiO_2$ impurity was selected for further investigation.

# Ce-pyrochlore: Phase diagram




Absence of $CeO_2$

Absence of Perovskite

$Ca_{0.670\pm0.034}Ce_{1.128\pm0.020}Ti_{2.194\pm0.034}O_{7\pm x}$

Energy

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# Ce-pyrochlore: Structural refinement

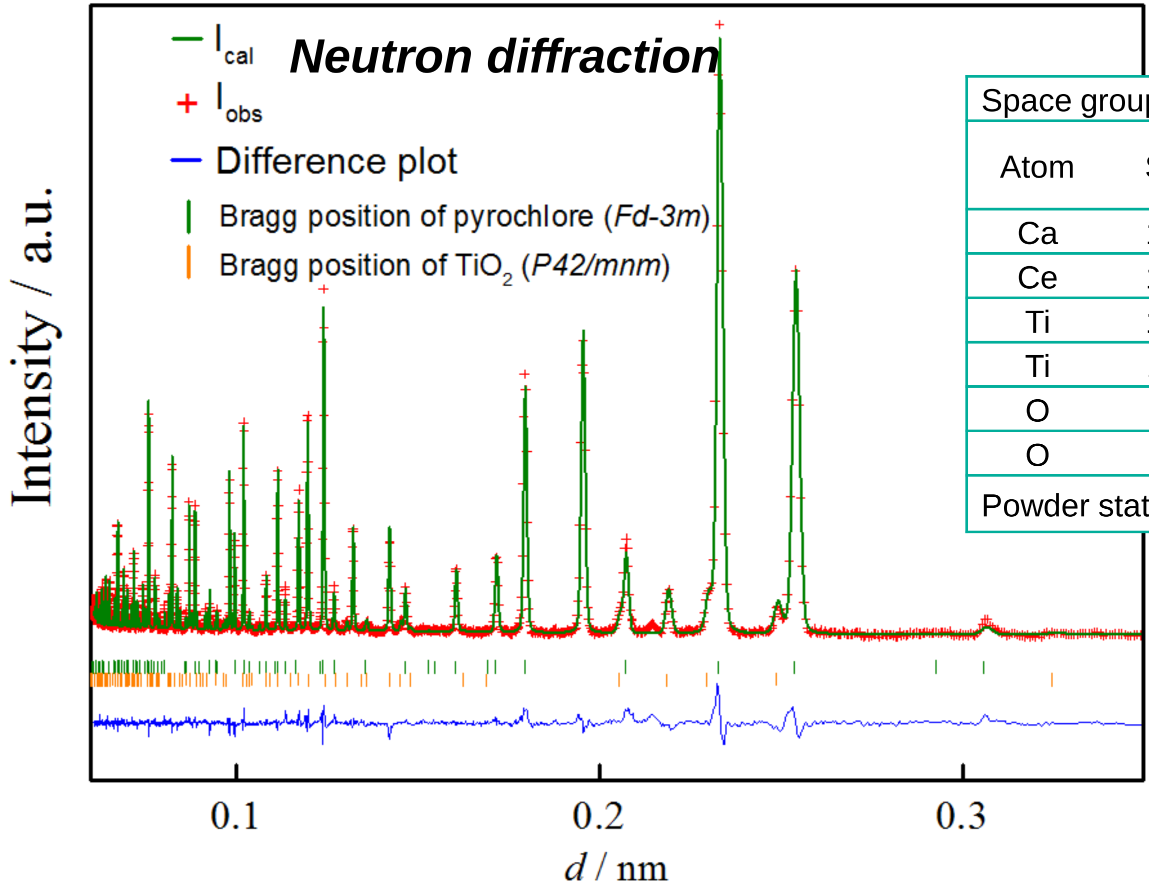



Table Refined structural parameters

| Space group: *Fd-3m* $a$ = 10.1462(4) Å | | | | | |
|---|---|---|---|---|---|
| Atom | Site | x | y | Z | $U_{iso}$ × 100(Å$^2$) |
| Ca | 16d | 0.5 | 0.5 | 0.5 | 0.532 |
| Ce | 16d | 0.5 | 0.5 | 0.5 | 0.532 |
| Ti | 16d | 0.5 | 0.5 | 0.5 | 0.532 |
| Ti | 16c | 0 | 0 | 0 | 0.859 |
| O | 48f | 0.3267 | 0.125 | 0.125 | 1.333 |
| O | 8b | 0.375 | 0.375 | 0.375 | 1.482 |
| Powder statistics: $\chi^2$ = 2.428 $R_{wp}$ = 5.48%, $R_p$ = 4.41% | | | | | |

## A site deficiency

B cation substitution on to the A cation lattice

Starting composition:

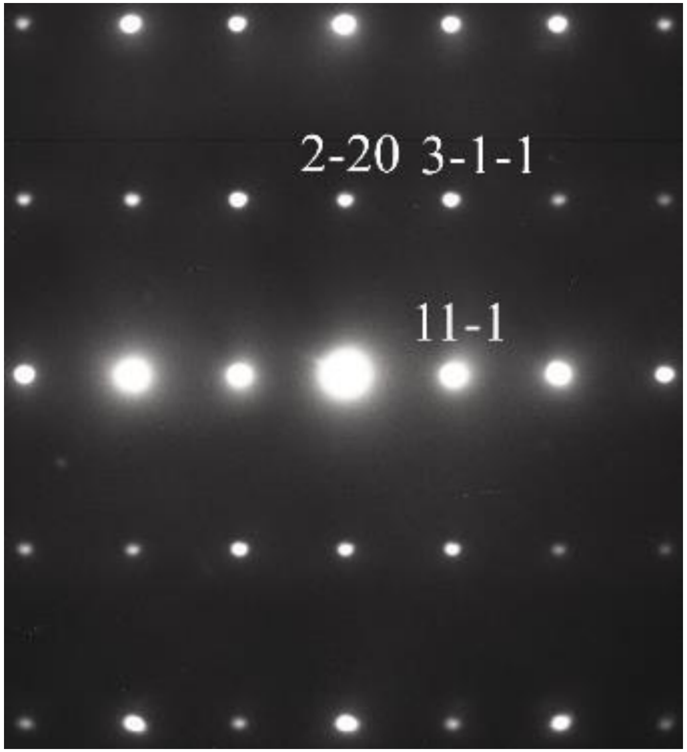
$Ca_{0.61}Ce_{1.08}Ti_{2.12}O_7$

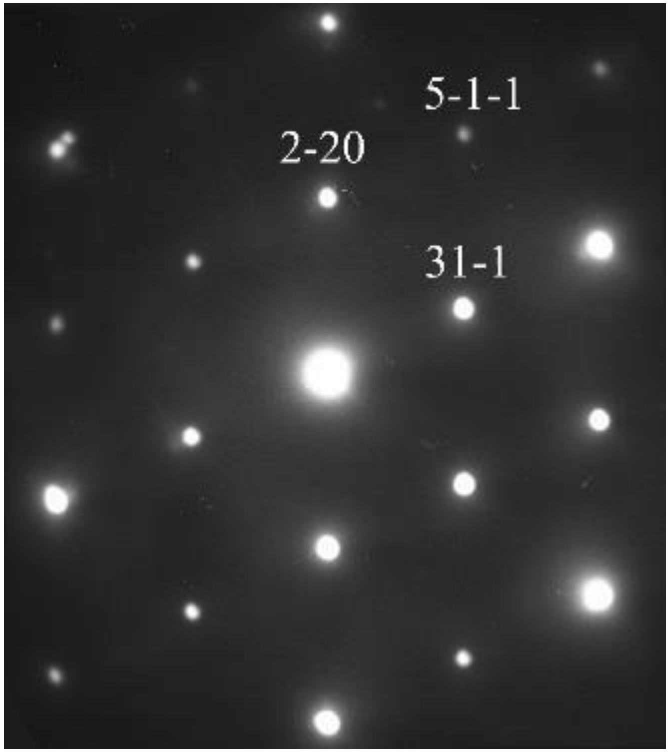
EDS composition:

$Ca_{0.60\pm0.04}Ce_{0.92\pm0.04}Ti_{2.27\pm0.04}O_7$

the ***first*** reliable structure determination on ND data of Ce-pyrochlore

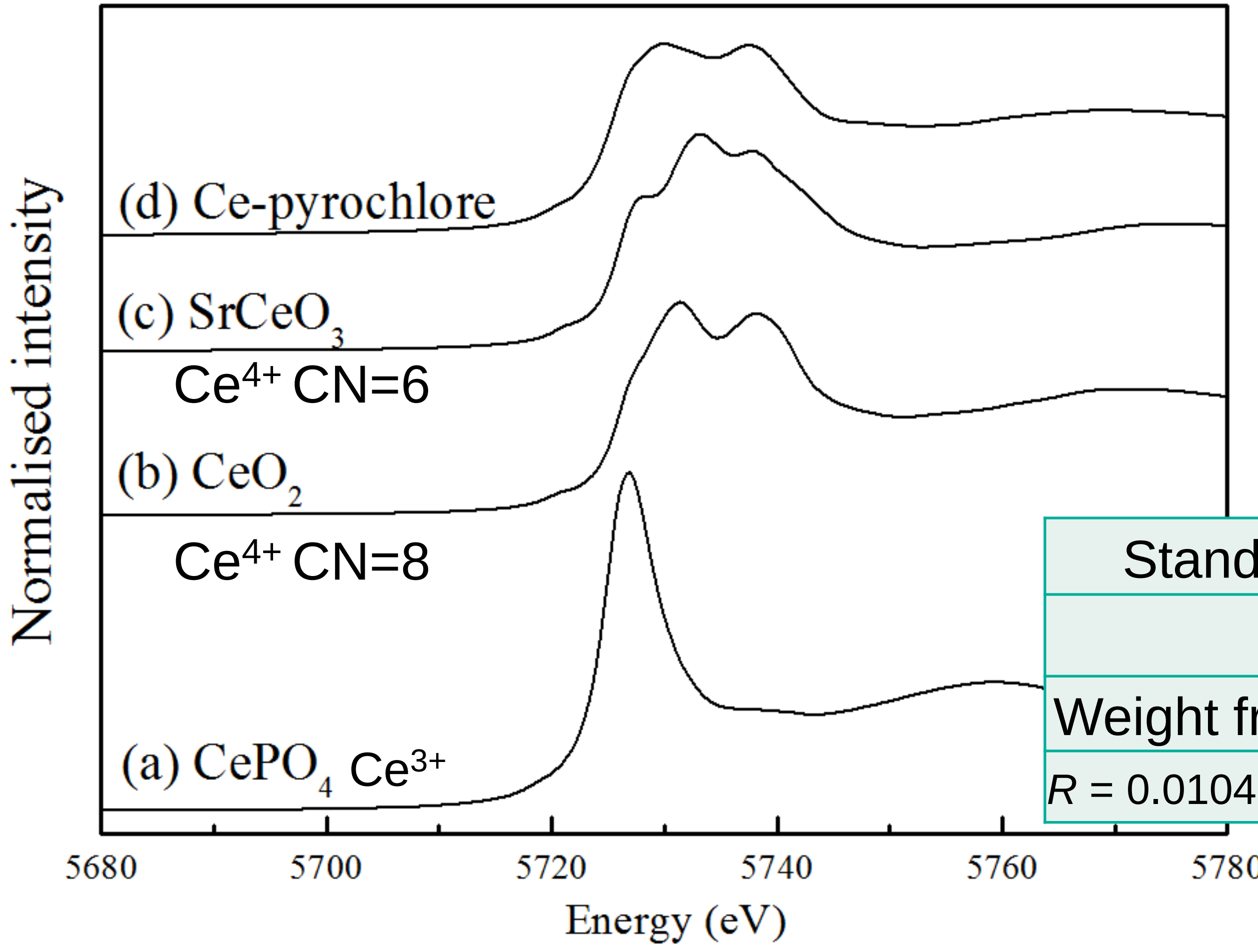
# Ce-pyrochlore: Electron diffraction




[112] and [114] zone axis diffraction patterns acquired from sample n ($Ca_{0.61}Ce_{1.08}Ti_{2.12}O_7$)

# Ce-pyrochlore: Oxidation state




$Ce^{4+}$ with CN = 8 was the dominant species in Ce-pyrochlore phase.

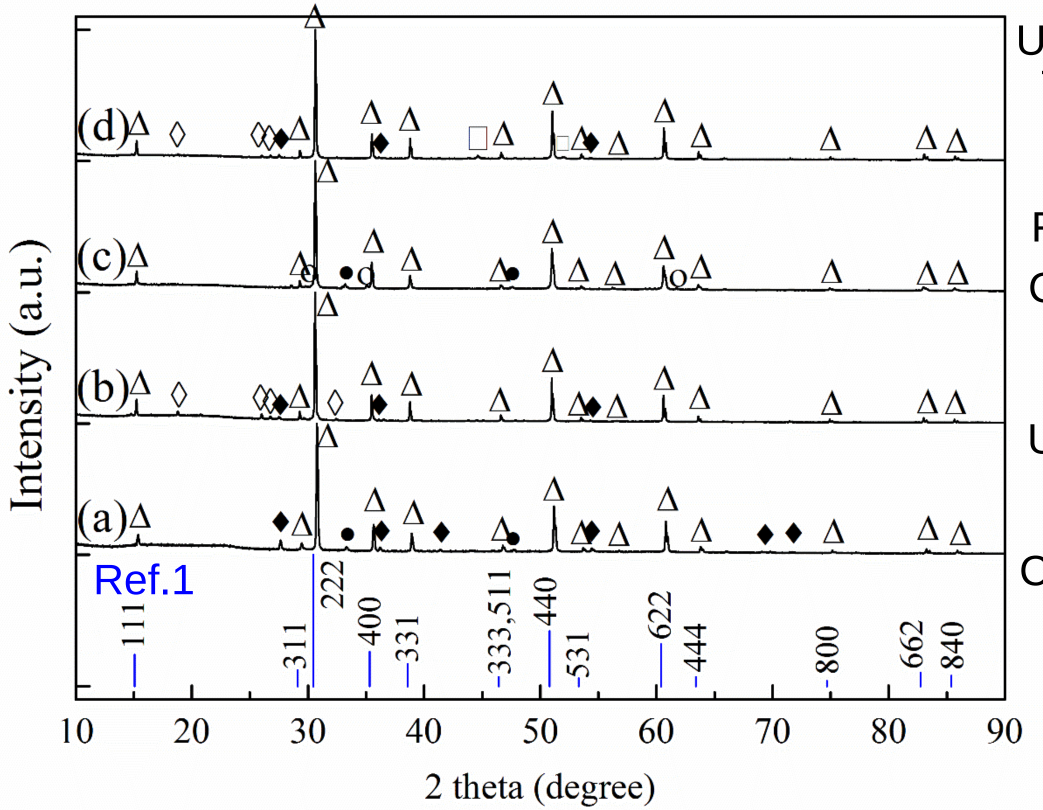
Linear combination fitting[1]

| Standard | $CeO_2$ | $CePO_4$ |
|---|---|---|
| | $Ce^{4+}$ | $Ce^{3+}$ |
| Weight fraction | 89.8 | 10.2 |
| $R$ = 0.0104 $\chi^2$=0.0037 | | |

3.9 v.u

1.using the program Athena
CN: Coordination number

# U-betafite: Phase assemblage




XRD patterns of the product after sintering of (a) U35, (b) U45, (c) U45Fe and (d) U45Ni.

*Impurity*

$UTi_2O_6$
$TiO_2$
Ni

$Fe_2TiO_4$
$CaTiO_3$

$TiO_2$
$UTi_2O_6$

$TiO_2$
$CaTiO_3$

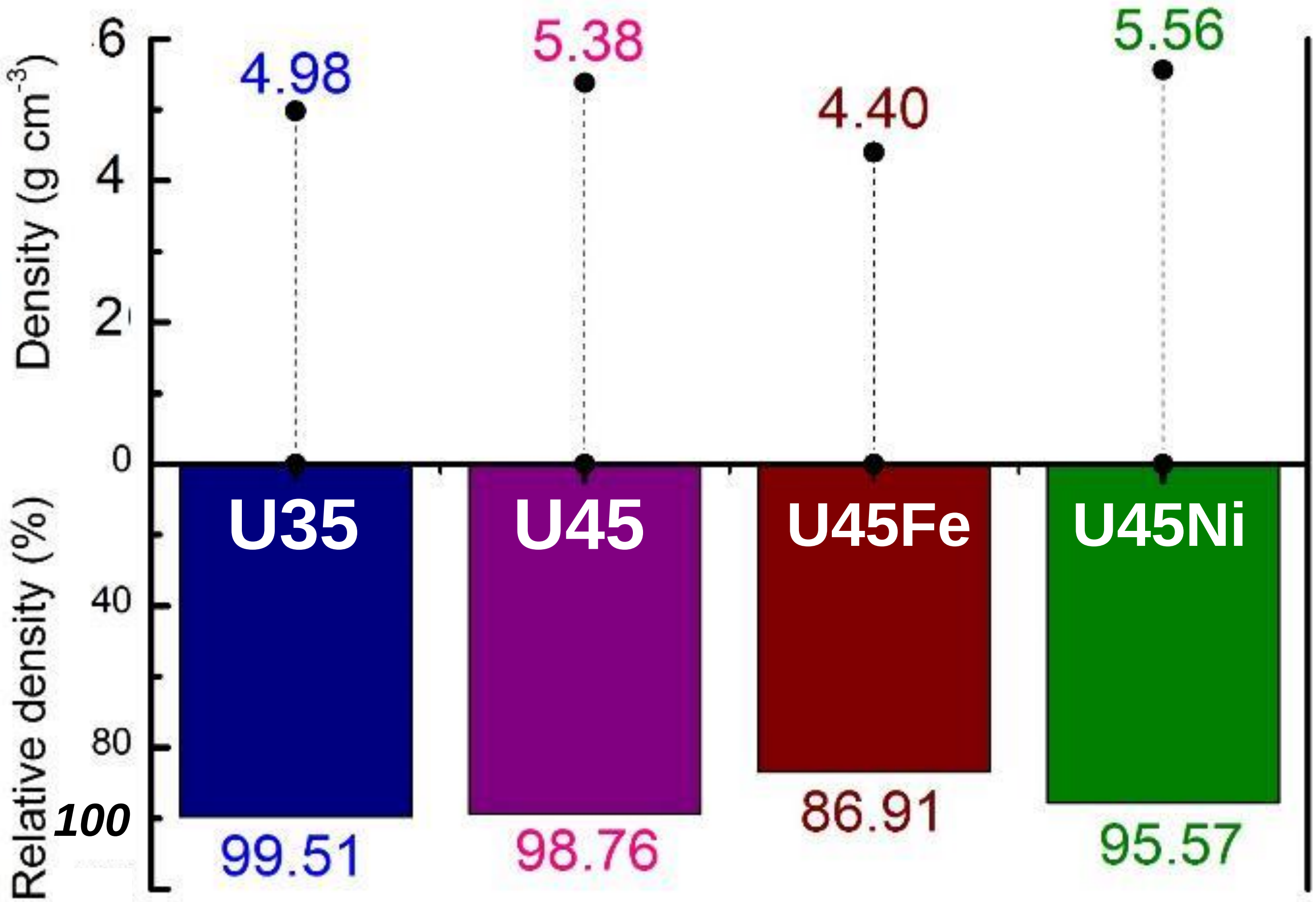
| **Sample** | **Betafite phase** Weight fraction (wt%)[2] |
|---|---|
| **U35** | 84.80 ± 0.24% |
| **U45** | 94.38 ± 0.07% |
| **U45Fe** | 86.42 ± 0.11% |
| **U45Ni** | 85.82 ± 0.11% |

No free U-oxides detected

A high betafite yield at relatively low temperature (1320$^{o}$C) in contrast to previous studies (< 75 wt% at 1450$^{o}$C, Ref. 3)


1. *J. Solid State Chem.*, **82** (1989) pp.146.
2. Determined by Rietveld QPA;
3. *J. Am. Ceram. Soc.*, 85 (2002) pp. 1853.

# U-betafite: Densification




Near fully-densification.

High sinterability.

Pure betafite phase but with significant porosity (RD ≈ 80%).[1]

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

# Conclusion

- An almost single phase Ce pyrochlore was synthesised and the first reliable structure determination was made.
- The betafite phase was obtained in high yield (> 85%); all $U_3O_8$ was incorporated into the ceramic host phase.

# Acknowledgements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# Thank you!