Understanding the Effectiveness of Plutonium Surrogates for Waste and Stockpile Immobilisation

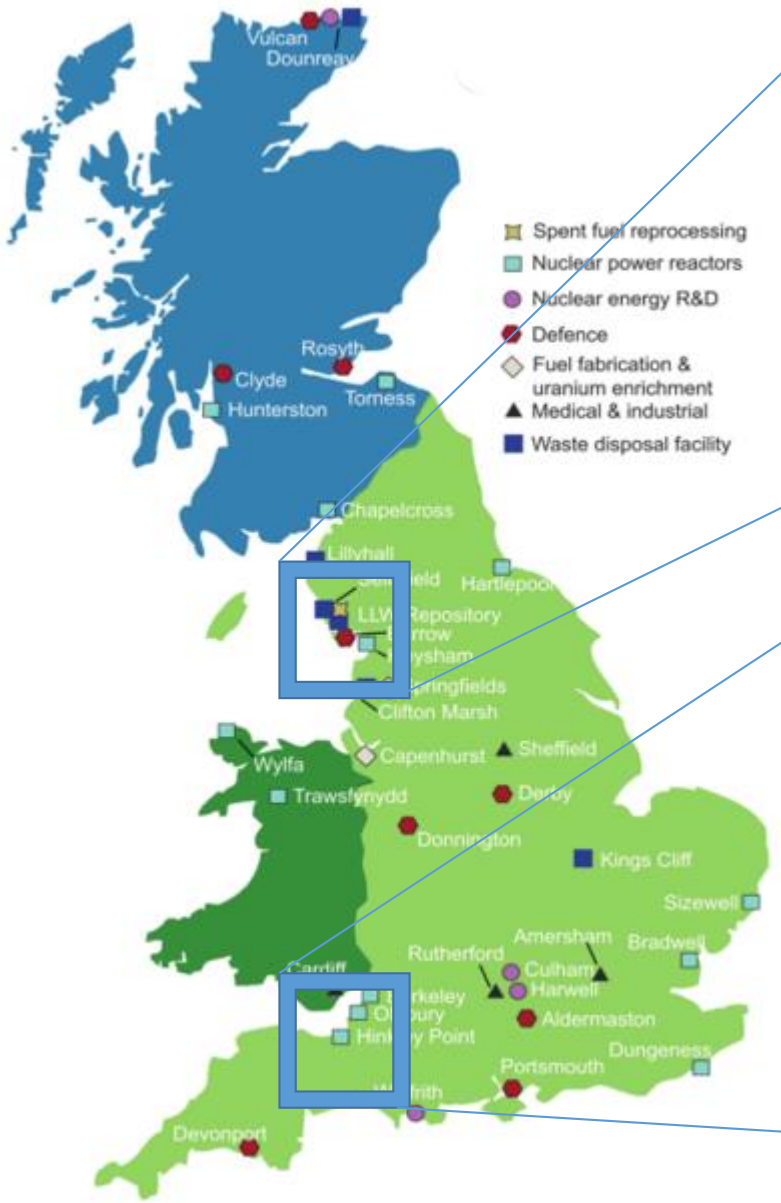
Lewis R Blackburn
Immobilisation Science Laboratory
University of Sheffield

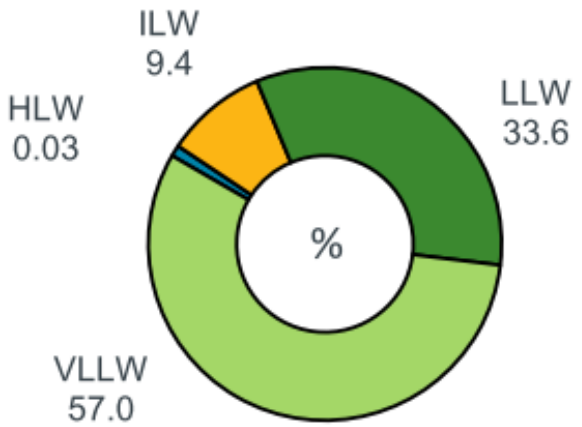
Supervisors:
- **Neil Hyatt (UoS)**
- **Martin Stennett (UoS)**
- **Ewan Maddrell (NNL)**

Joint ICTP-IAEA International School on Nuclear Waste Actinide Immobilization
Trieste 2018

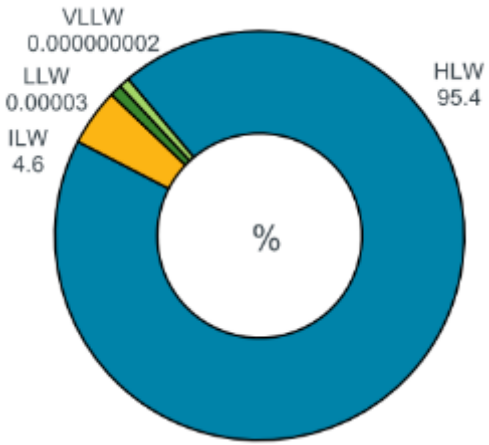
Radioactive Waste in the United Kingdom

The University Of Sheffield.



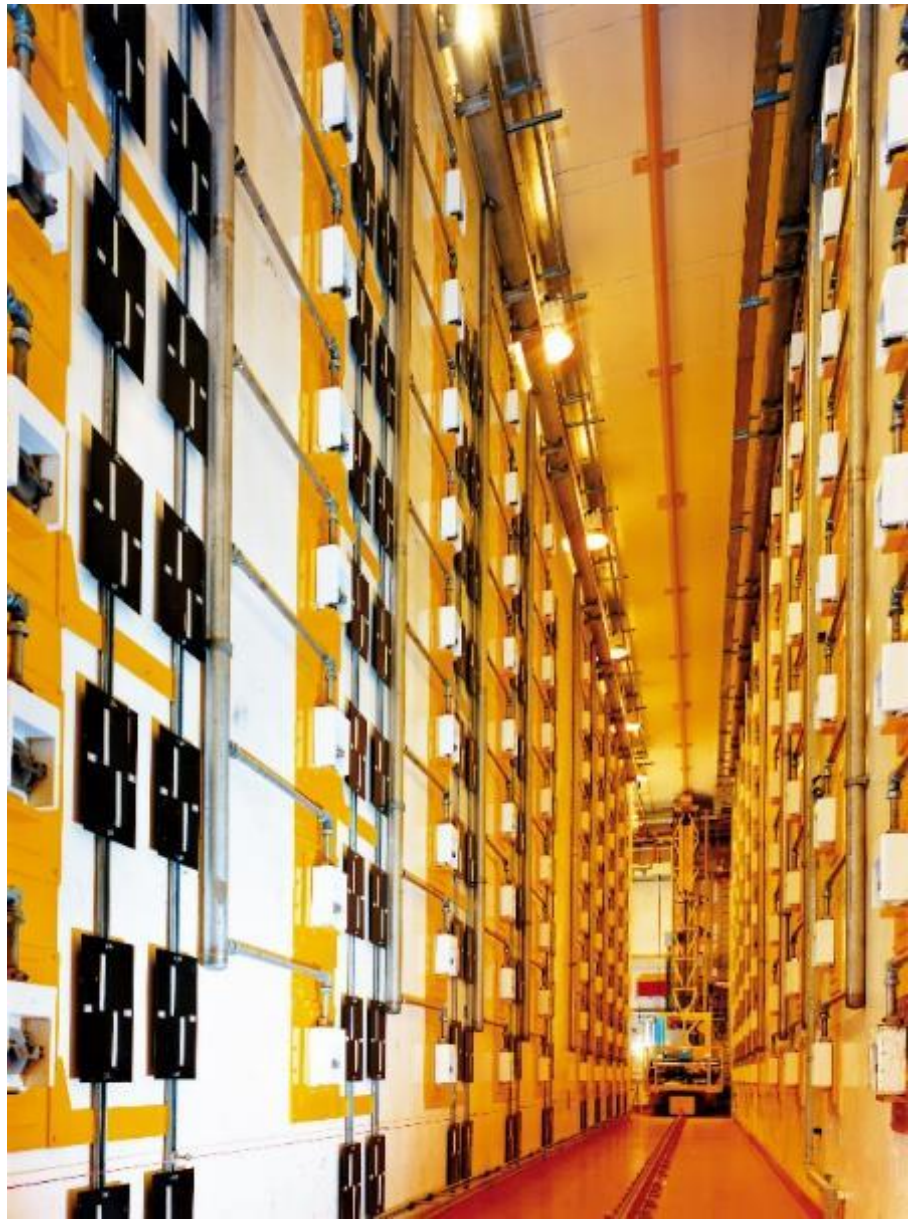


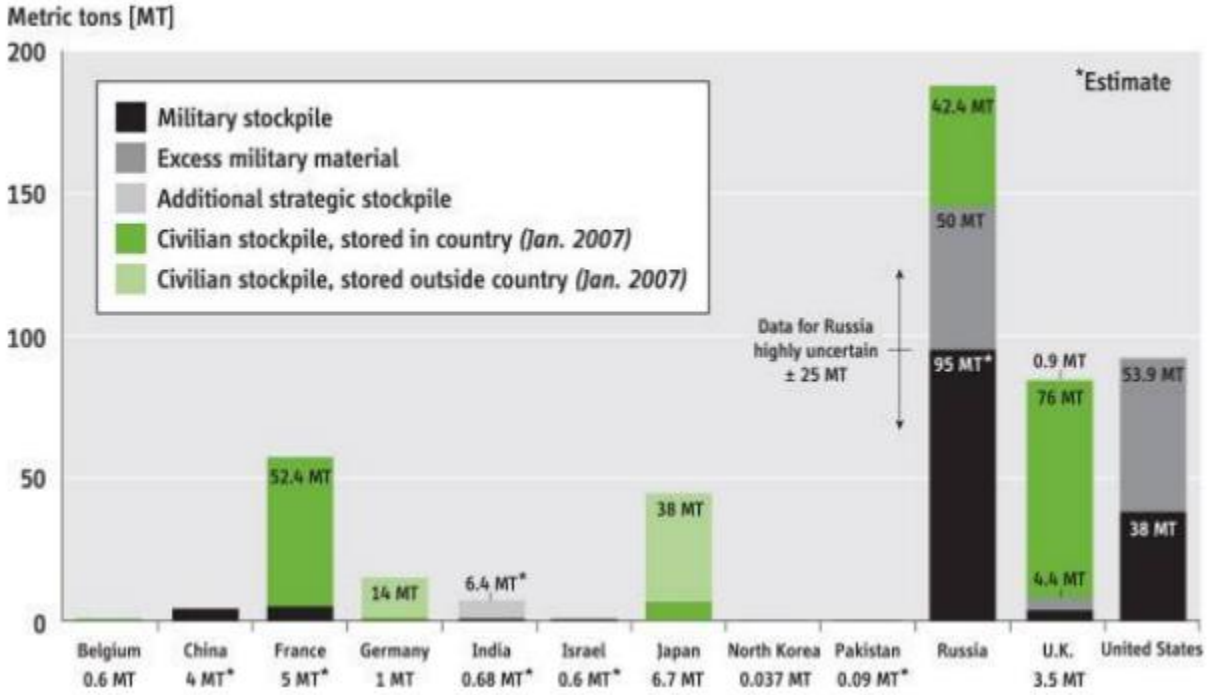
Total packaged volume = 4,770,000 m³



Total activity = 83,000,000 TBq

United Kingdom Plutonium Stocks





- The United Kingdom reprocesses spent nuclear fuel into reusable components *via* PUREX separations, this takes place at ThORP (Thermal Oxide Reprocessing Plant), Sellafield.
- Reprocessing will cease in 2018; UK plutonium stocks are predicted to reach **140 teHM** (largest non-military stockpile worldwide.
- The Nuclear Decommissioning Authority (NDA) is liable for the stockpile and is in the process of refining several credible options for long term management.

Dual Track Strategy

Contents lists available at ScienceDirect

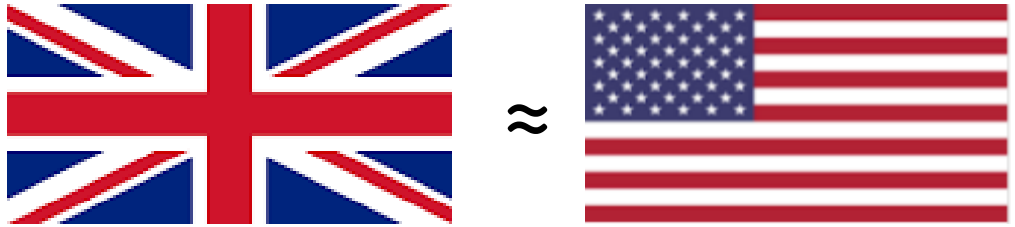
Energy Policy

journal homepage: www.elsevier.com/locate/enpol

Plutonium management policy in the United Kingdom: The need for a dual track strategy

Neil C. Hyatt

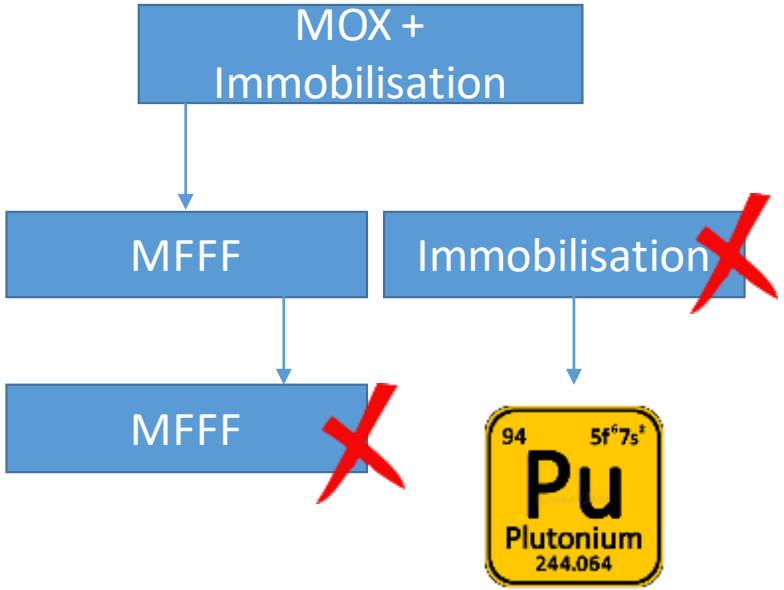
Immobilisation Science Laboratory, Department of Materials Science and Engineering, The University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, UK



- Almost 40 t of separated plutonium left without disposition route
- Comparisons between UK and US positions
- Indicates MOX based strategy might not be sustainable or achievable

MOX Fuel Fabrication Facility

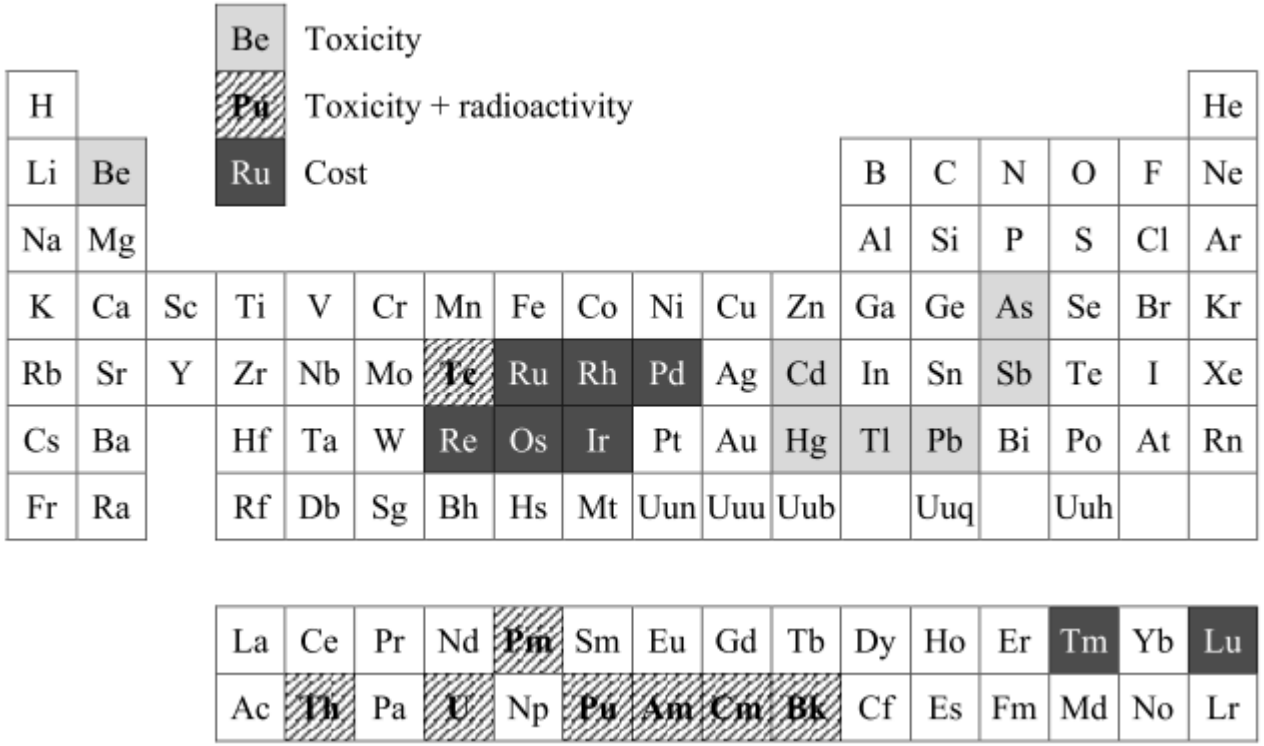
- $4,000,000,000 and 50% complete
- Cost and schedule overruns
- Inadequate assumptions of labour and equipment
- Projected to cost around $30,000,000,000
- ‘Stranded Plutonium’



Dual Track Strategy:

- Immobilisation and disposal to spearhead policy
- Regressions to MOX programme would not strand the Pu without disposition route
- *“any remaining plutonium which is not converted to MOX, or otherwise reused, will be immobilised and treated as waste for disposal.”*

The use of surrogates/simulants is common:



- Some elements are costly and radioactive
- Stringent requirements for Pu manipulation
- Specialist equipment and risk to workers

SURROGATE HEIRARCHY

58
Ce
Cerium
140.12

- Most widely used
- Lanthanide
- Cheap

92
U
Uranium
238.03

- Most similar to Pu
- Radiotoxic
- Handling requirements

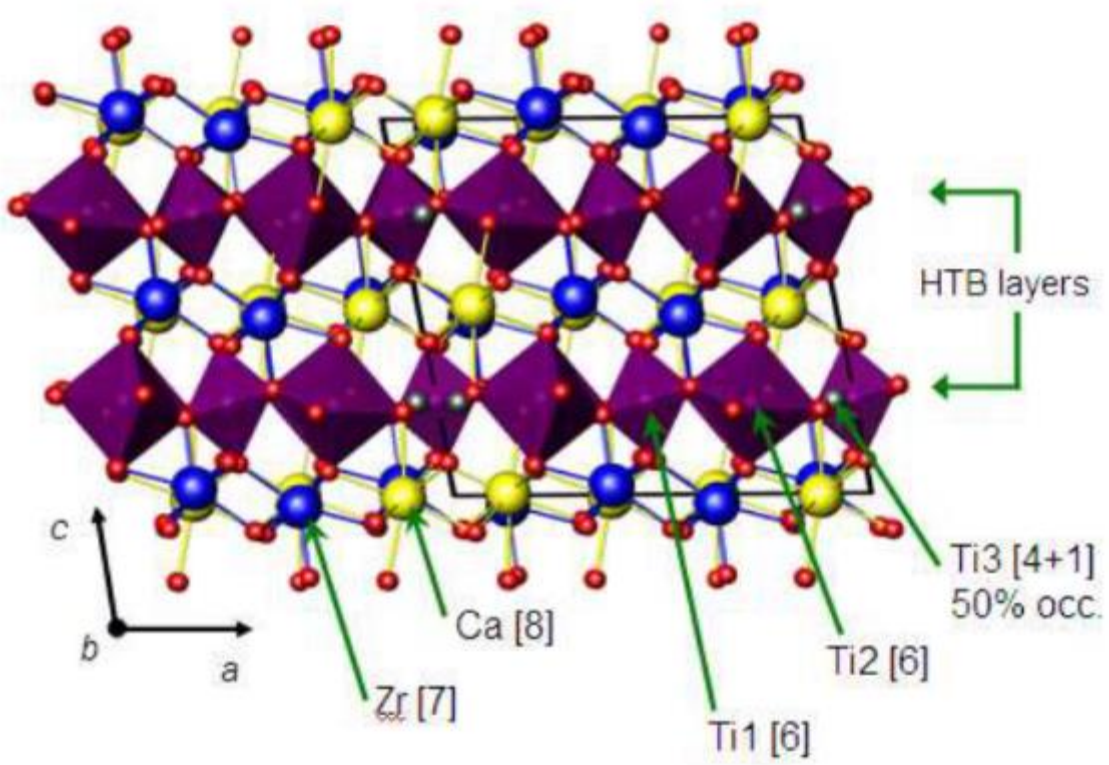
90
Th
Thorium
232.04

- Actinide
- Least studied
- Gap in knowledge?

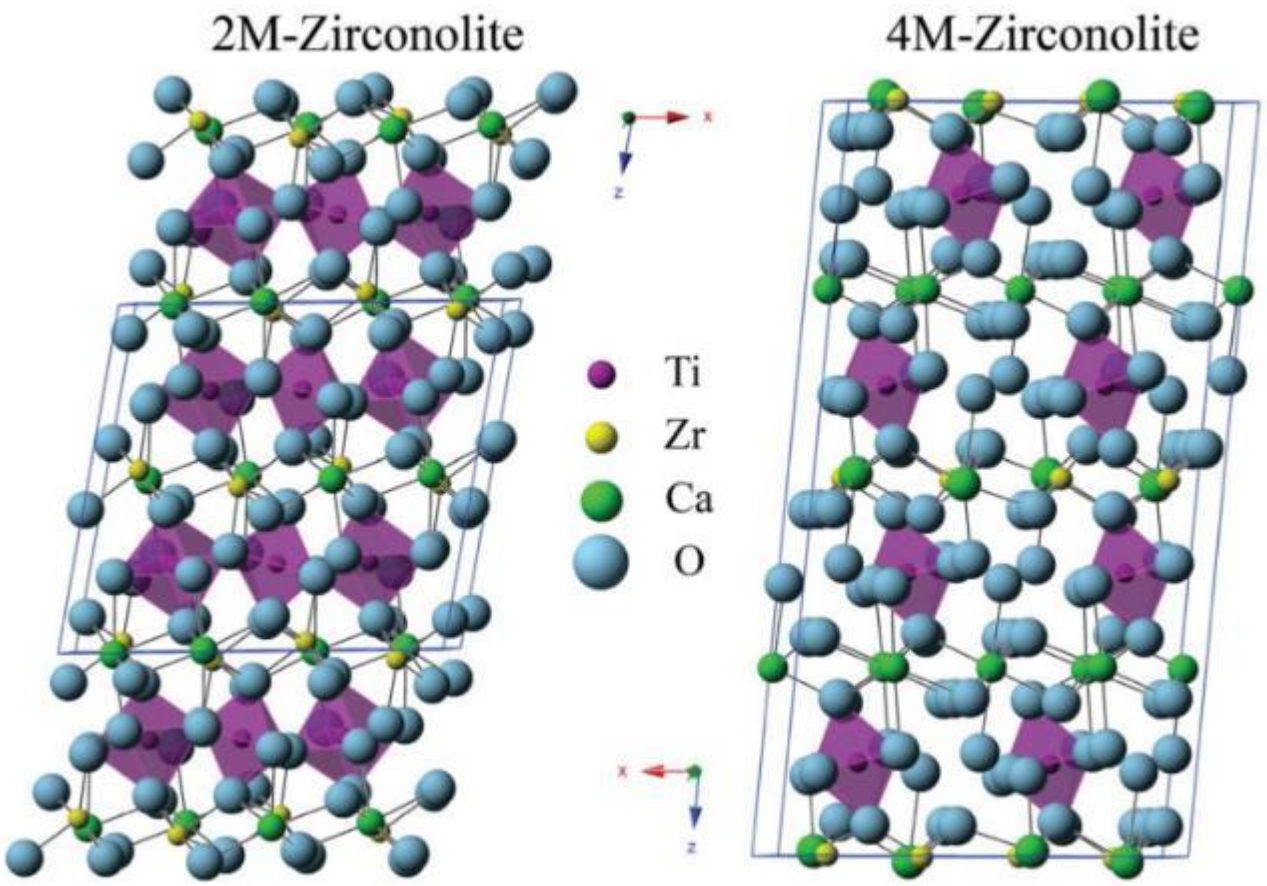
ATTENTION

No element can successfully provide a full suite of behaviours from which true mimicking can occur

$CaZrTi_2O_7$ Zirconolite



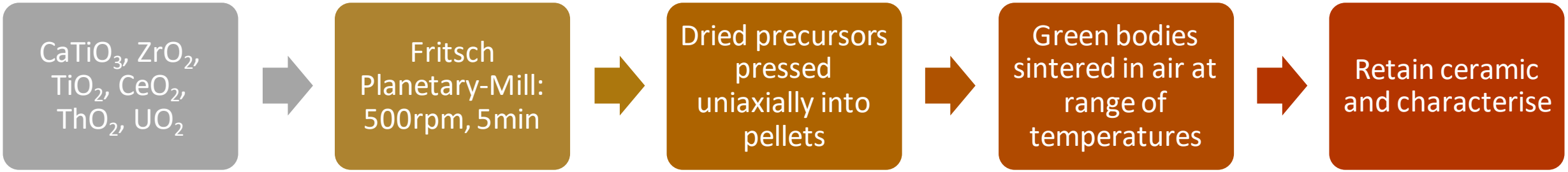
Composition	Wt%	Mineralogy	Wt%
TiO_2	57.0	Hollandite	30
ZrO_2	5.4	Zirconolite	30
Al_2O_3	4.3	Perovskite	20
BaO	4.4	Magnéli phases	15
CaO	8.9	Intermetallics	5
HLW	20.0		



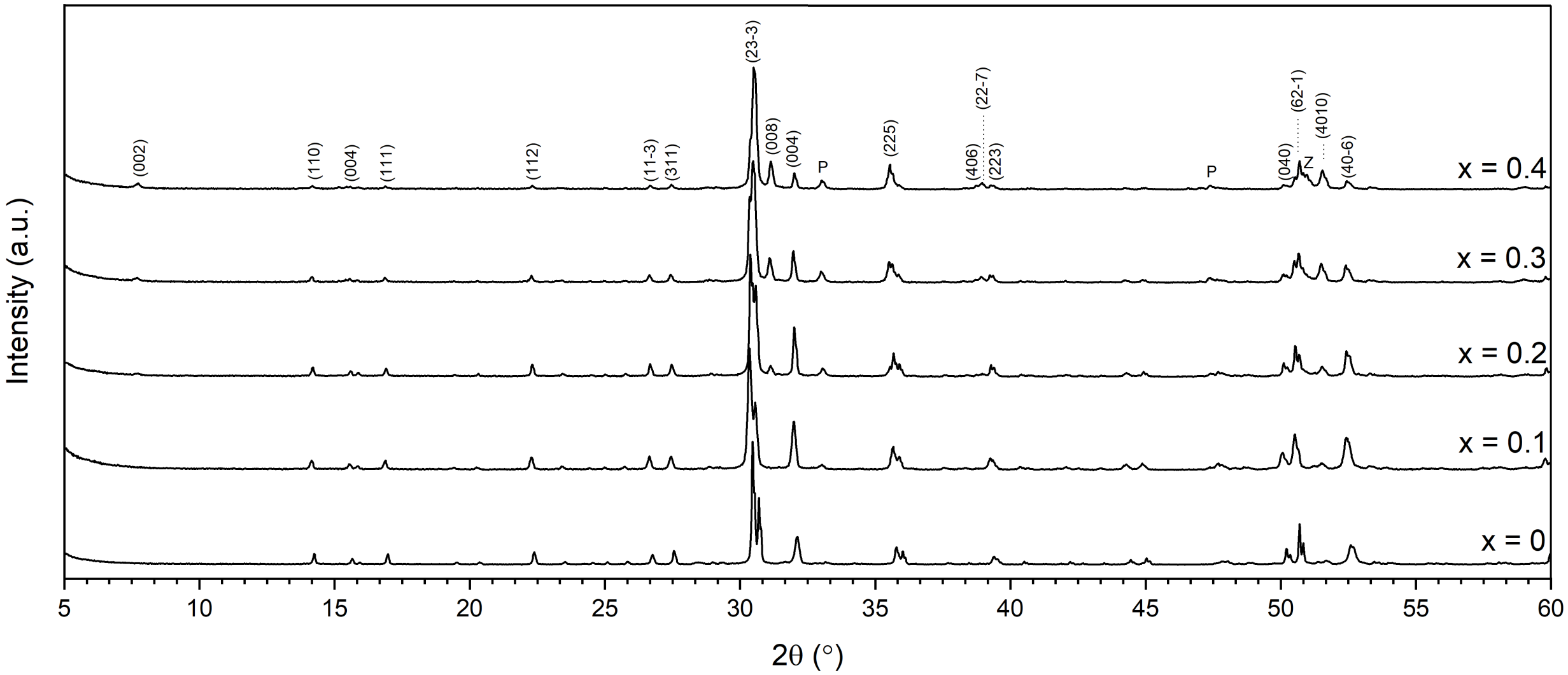
- Candidate phase for plutonium retention: Synroc-C
- Demonstrated aqueous durability
- Natural analogues
- Waste ions can partition onto both Zr^{4+} and Ca^{2+} sites
- Polytypic behaviour (2M, 4M, 3T etc.)

- Compare relative behaviour of plutonium surrogates Ce, U, Th, by incorporation into zirconolite lattice
- Synthesised materials characterised by XRD, SEM, EDX, XAS

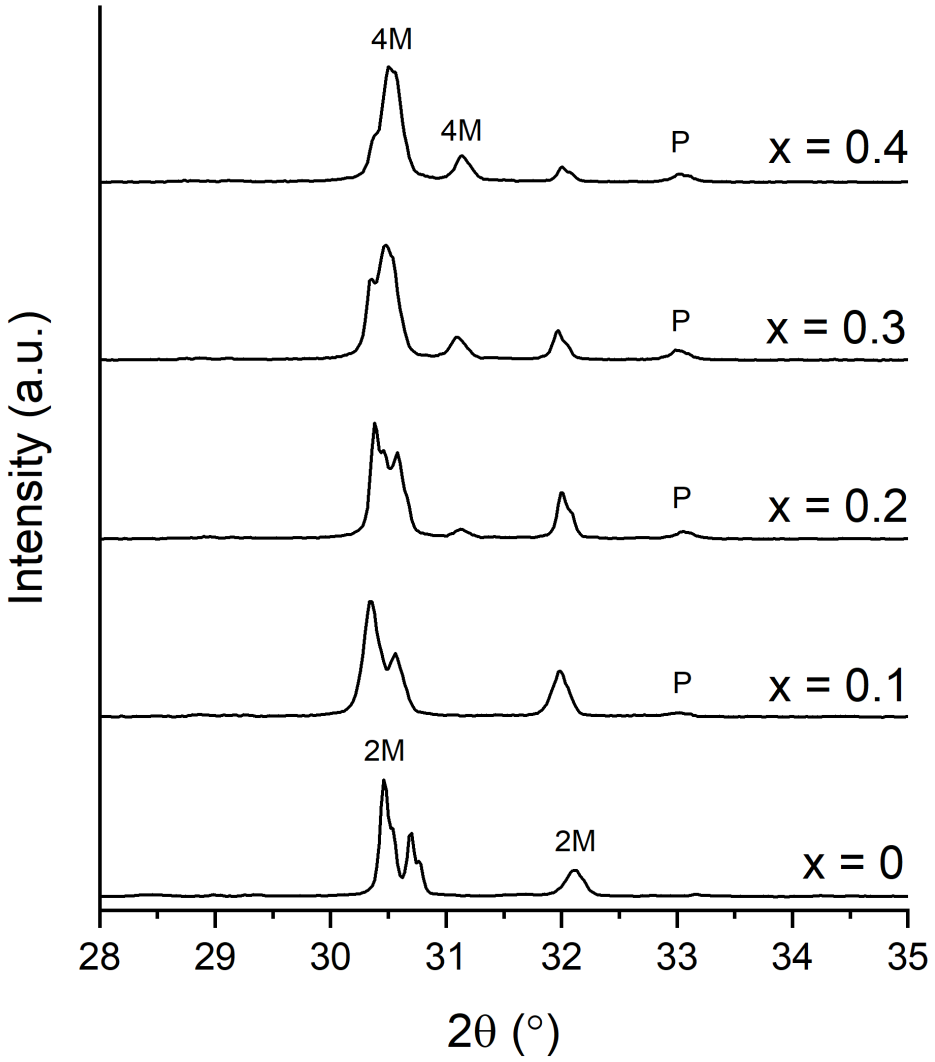
Target Composition (S_x = U^{4+}, Th^{4+}, Ce^{4+})	Target Valence
$CaZr_{0.6}S_{0.4}Ti_2O_7$	+4
$CaZr_{0.7}S_{0.3}Ti_2O_7$	+4
$CaZr_{0.8}S_{0.2}Ti_2O_7$	+4
$CaZr_{0.9}S_{0.1}Ti_2O_7$	+4

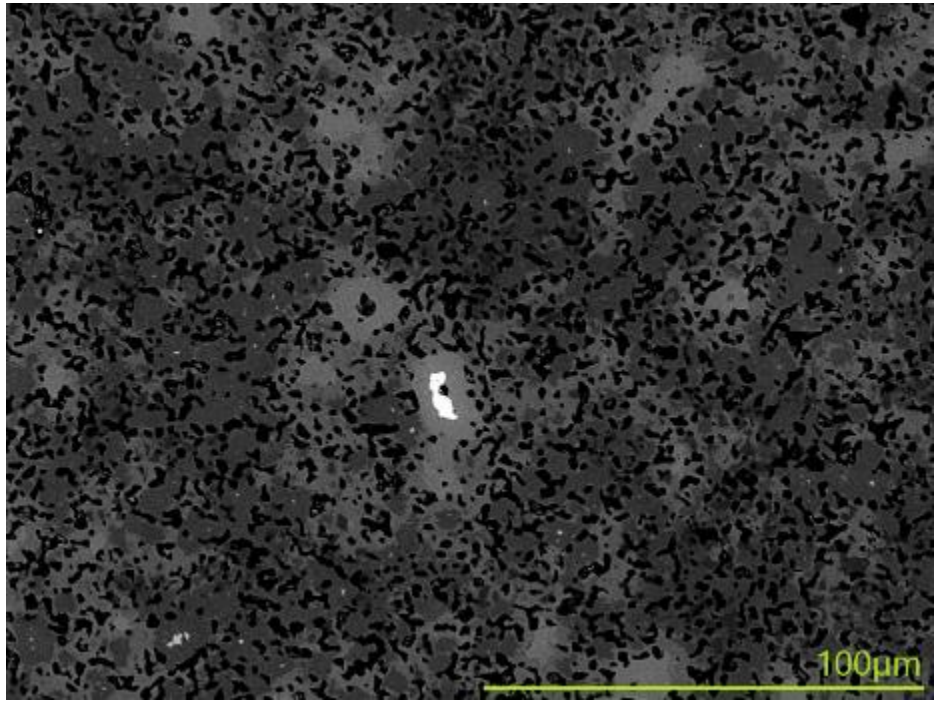


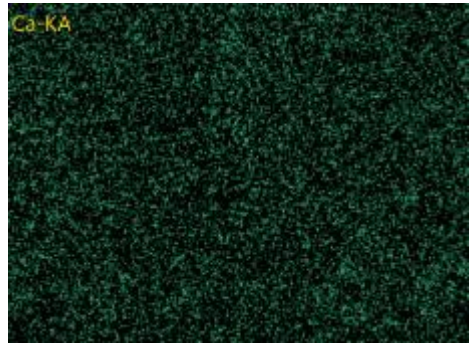
$CaZr_{1-x}Ce_xTi_2O_7$ – 1300°C, 8 h

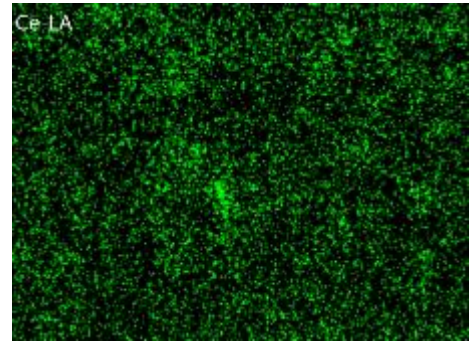


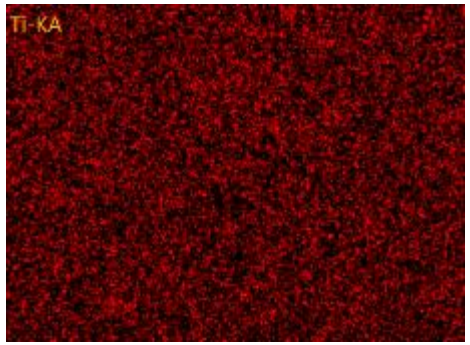
$CaZr_{1-x}Ce_xTi_2O_7$ – 1300°C, 8 h

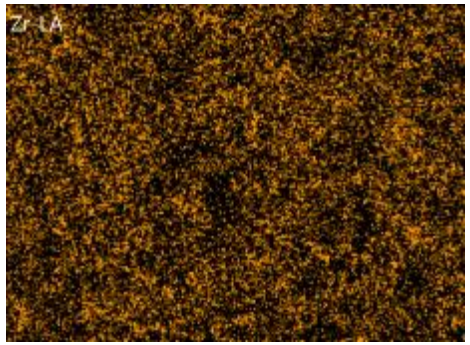




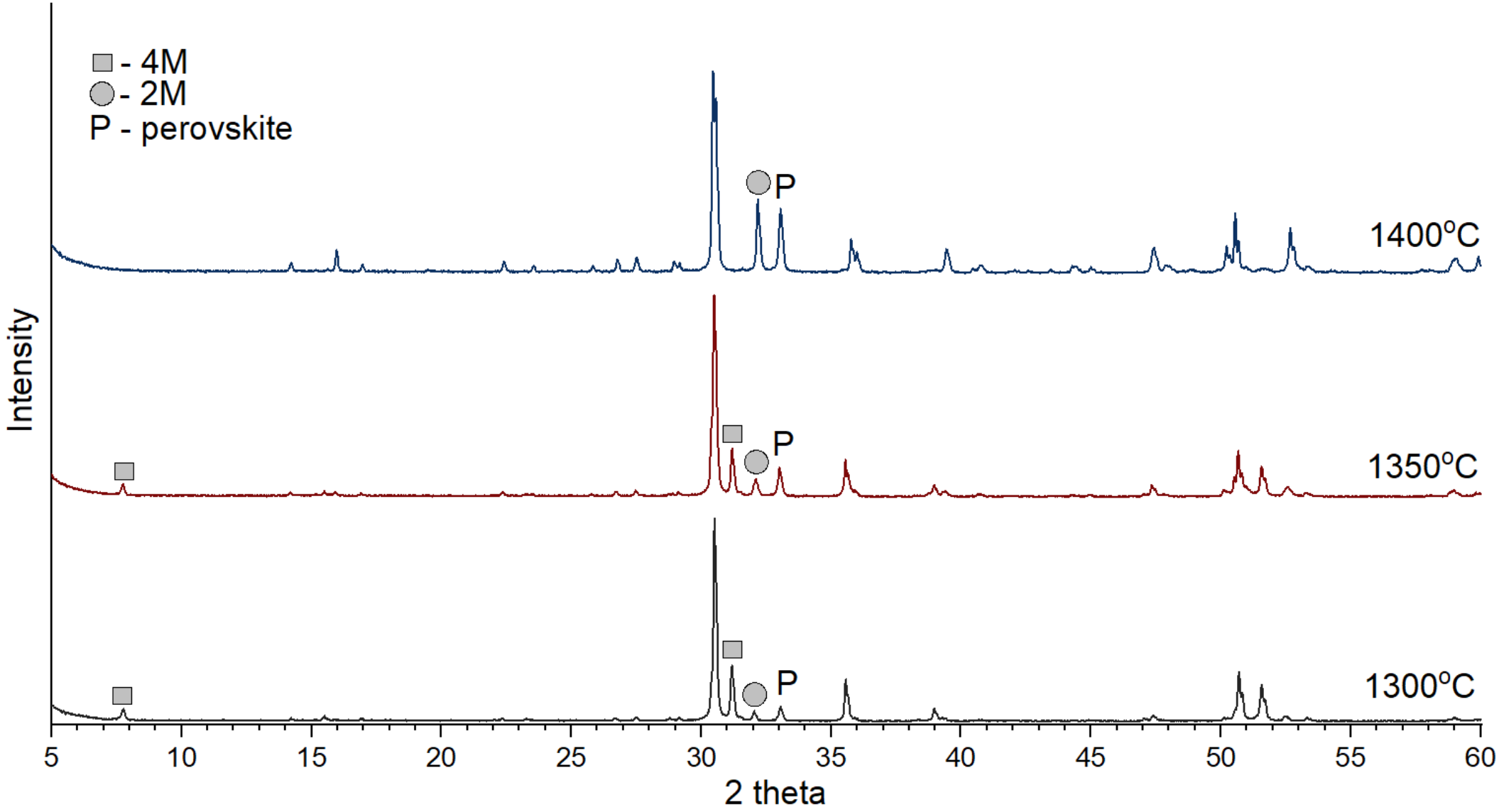




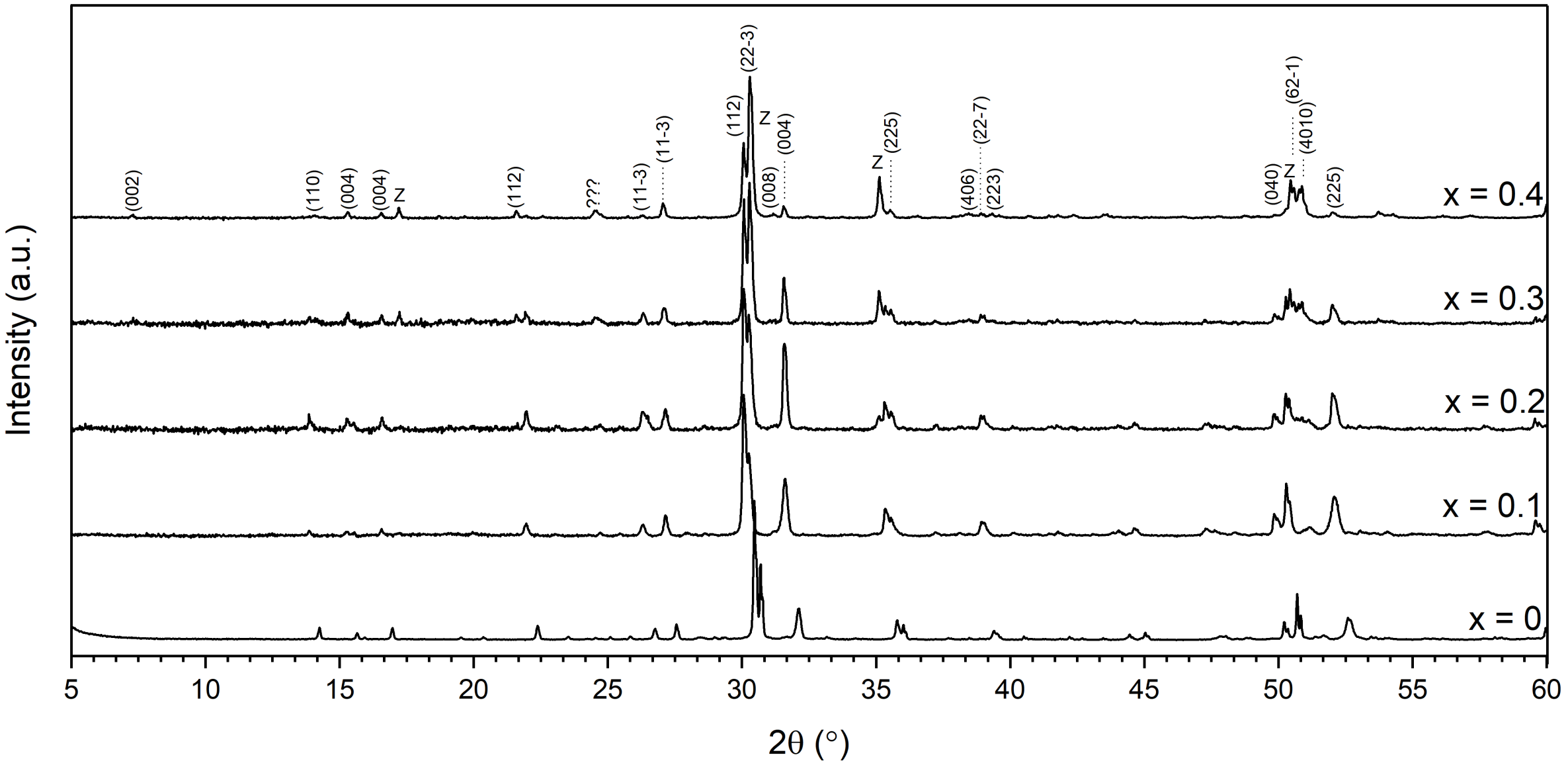


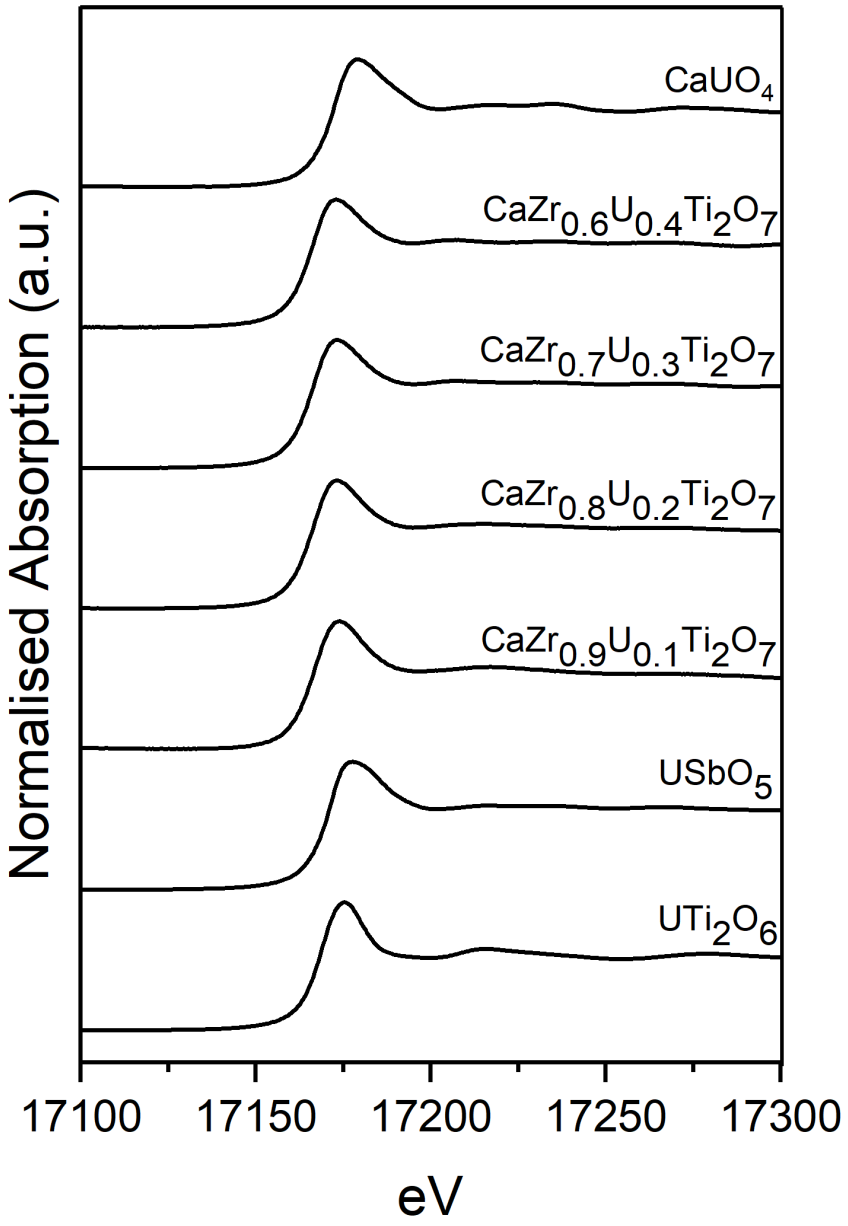


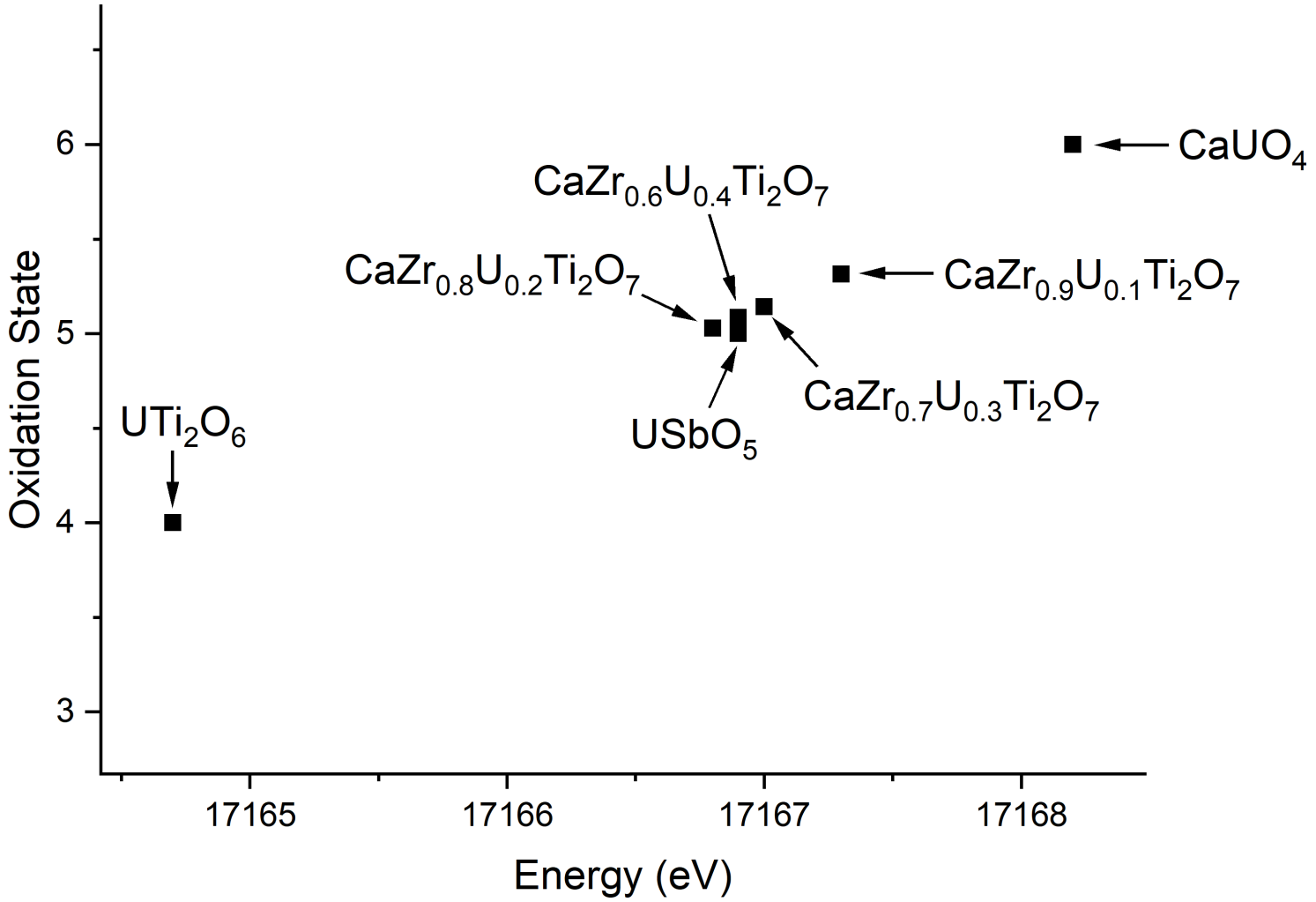
$CaZr_{0.6}Ce_{0.4}Ti_2O_7$ – 12 h



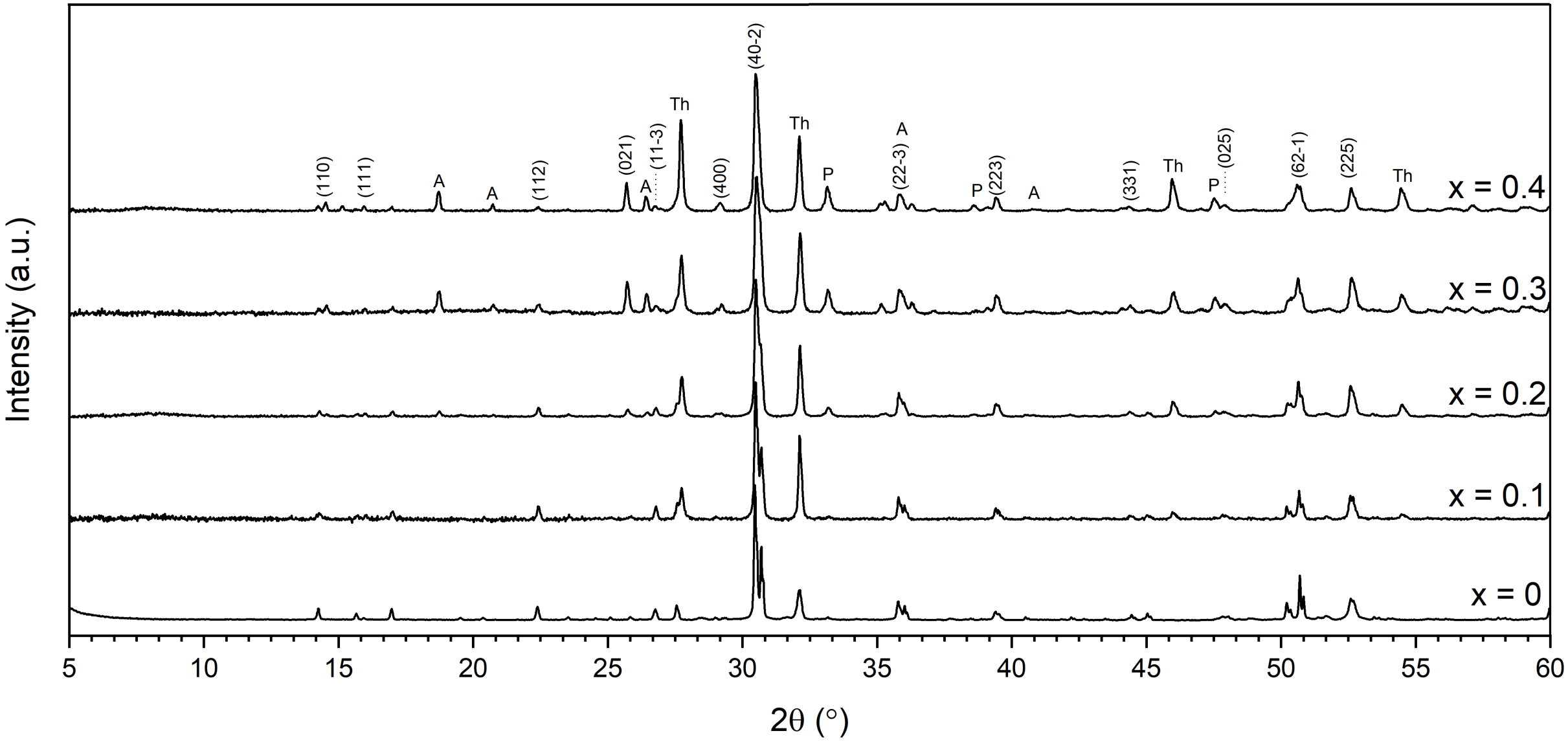
XRD – $CaZr_{1-x}U_xTi_2O_7$



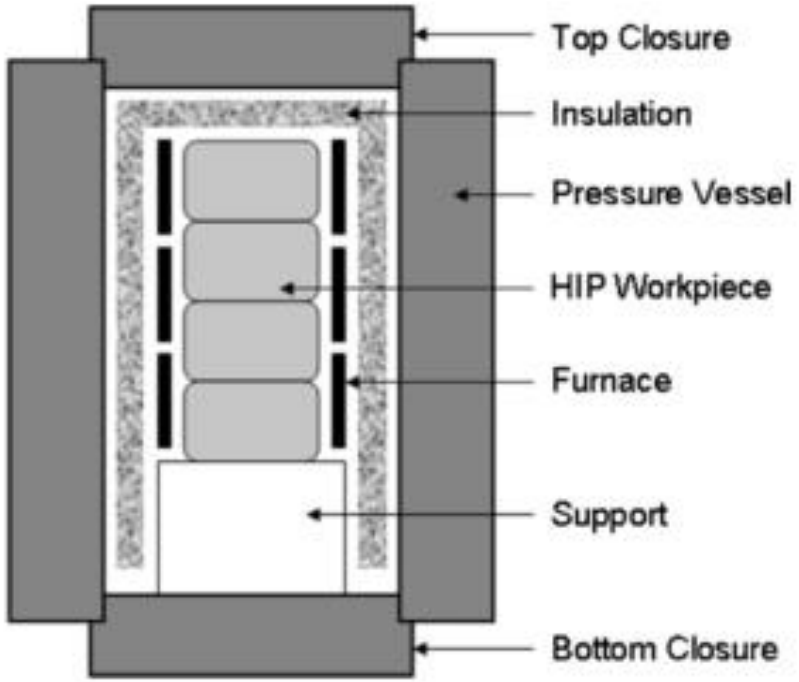

Normalised Absorption (a.u.)
CaUO4
CaZr0.6U0.4Ti2O7
CaZr0.7U0.3Ti2O7
CaZr0.8U0.2Ti2O7
CaZr0.9U0.1Ti2O7
USbO5
UTi2O6
17100
17150
17200
17250
17300
eV

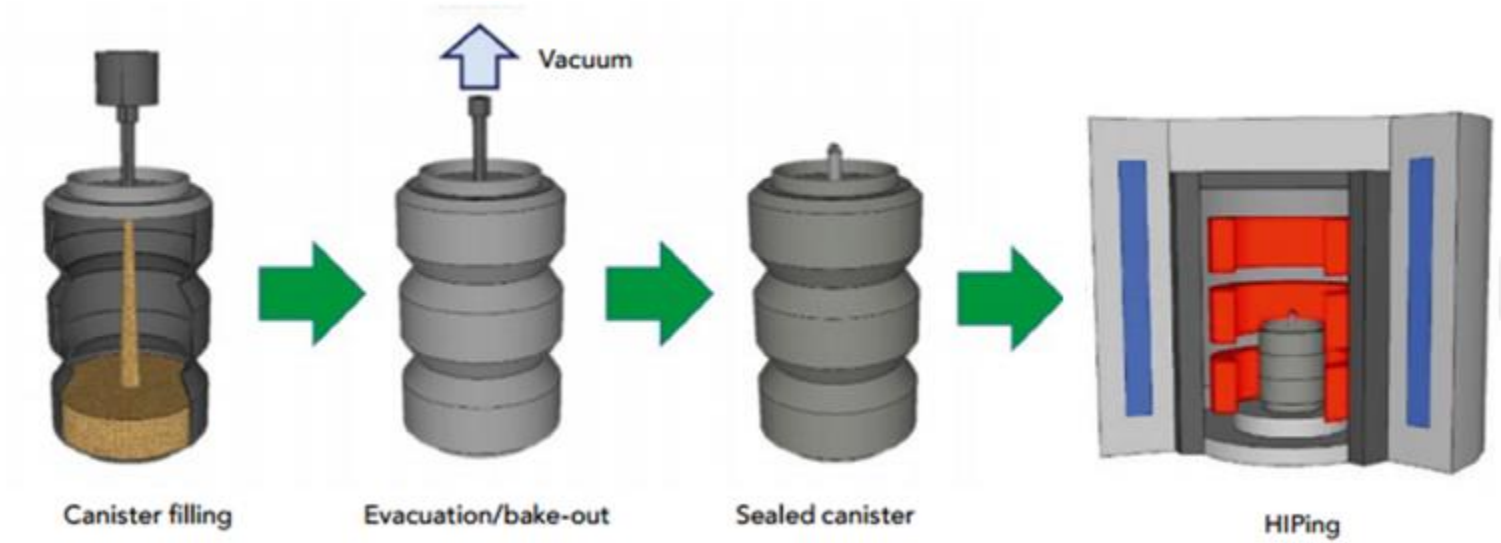

Oxidation State
6
5
4
3
CaUO4
CaZr0.6U0.4Ti2O7
CaZr0.8U0.2Ti2O7
CaZr0.9U0.1Ti2O7
CaZr0.7U0.3Ti2O7
USbO5
UTi2O6
17165
17166
17167
17168
Energy (eV)

XRD – $CaZr_{1-x}Th_xTi_2O_7$



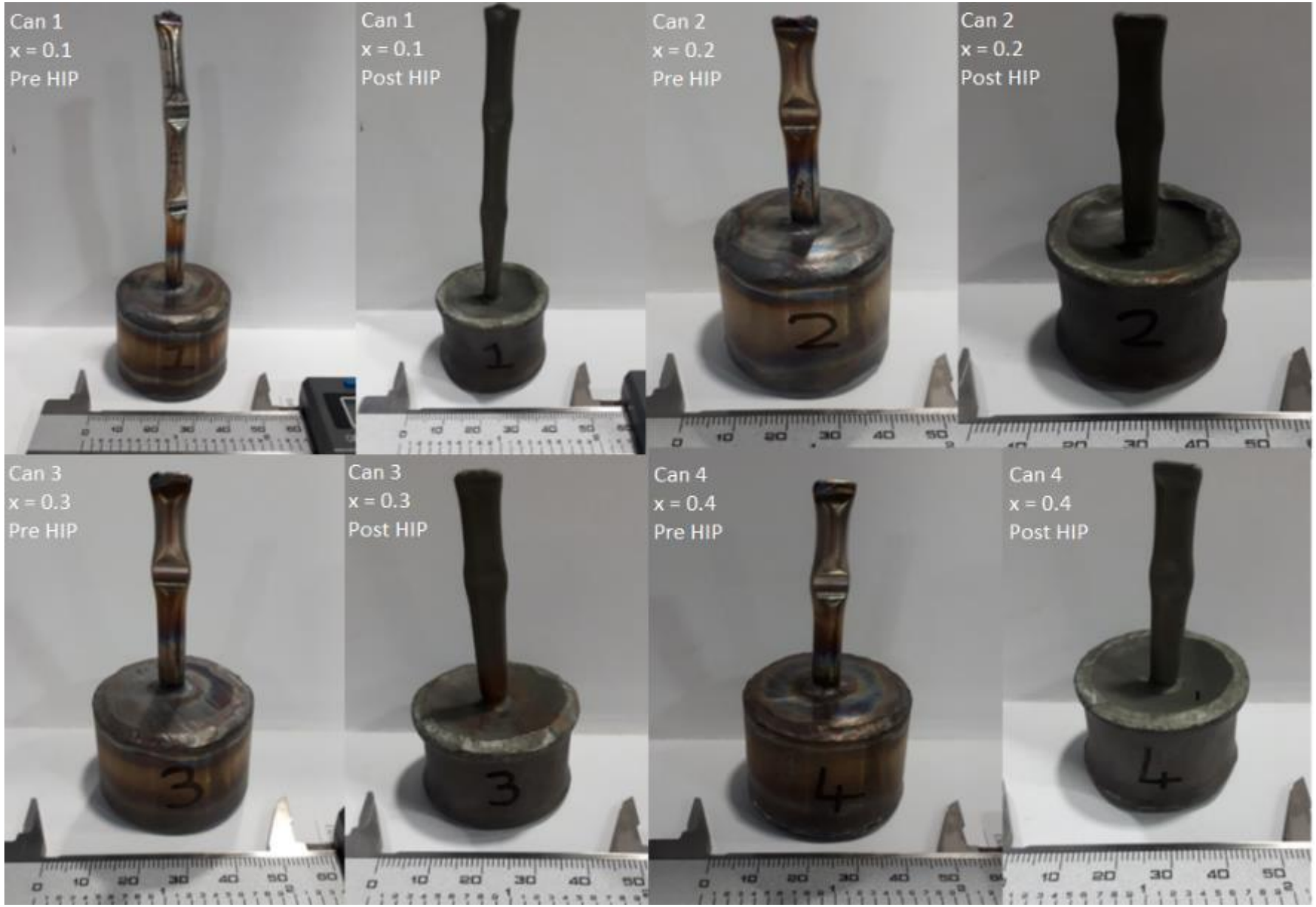
Hot Isostatic Pressing: $CaZr_{1-x}Ce_xTi_2O_{7.}$ x = 0.1, 0.2, 0.3, 0.4





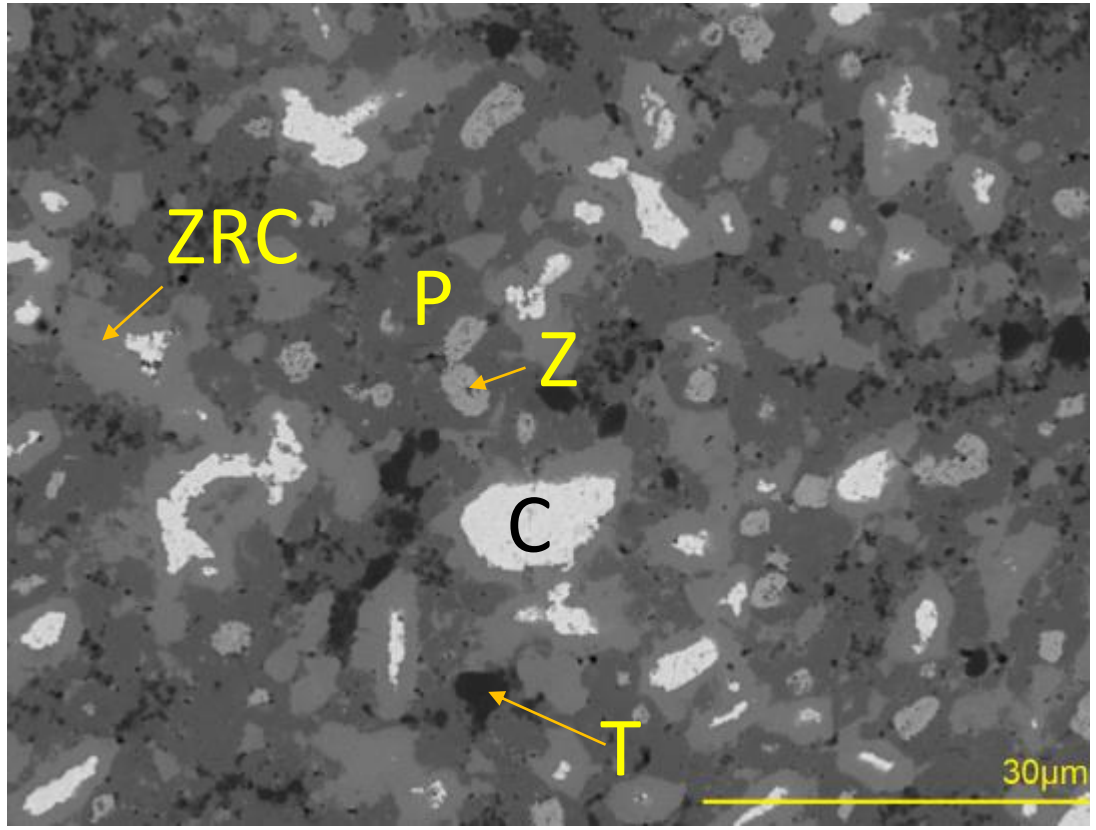
55g batch: $CaTiO_3$, ZrO_2, TiO_2, CeO_2 → Fritsch Planetary-Mill: 500rpm, 10min → 600°C 12h calcine → Evacuation + 300° 14h bake-out → HIP: 10°C/min ramp, 1200°C, 100MPa, 4h → Retain ceramic and characterise

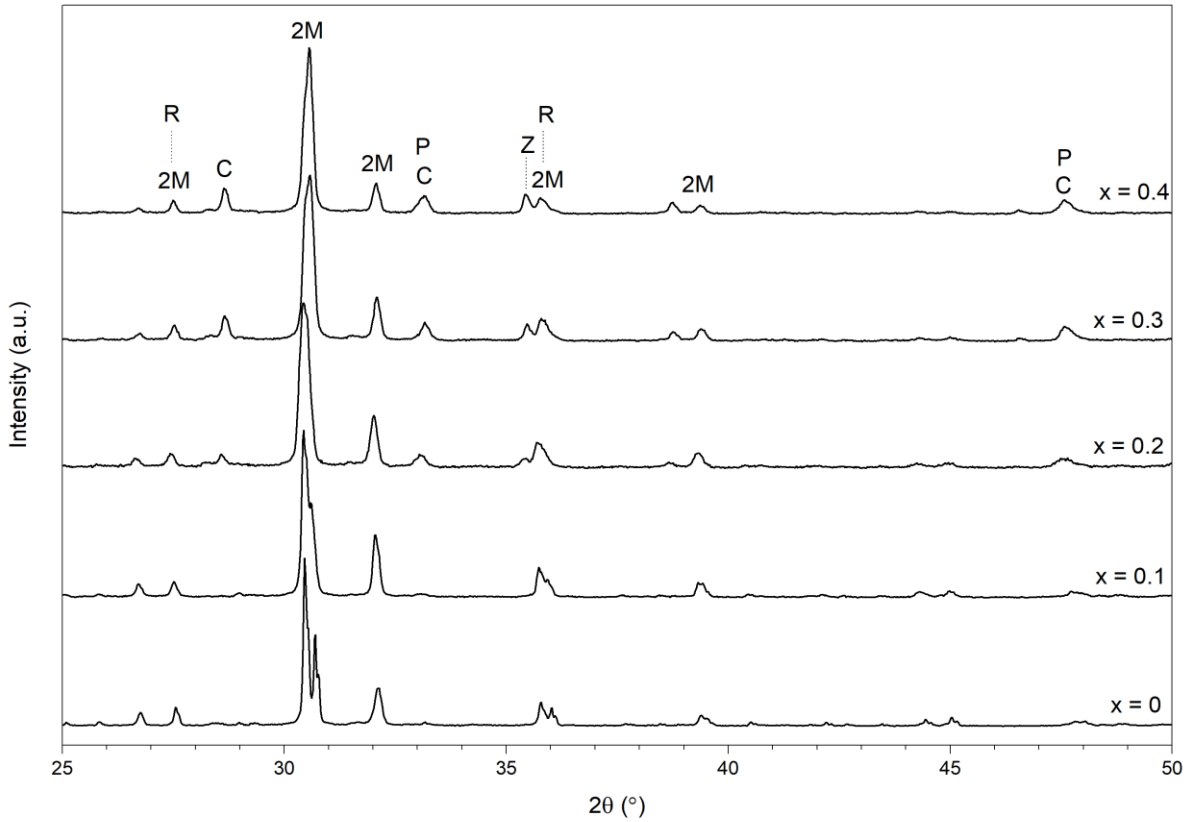
Hot Isostatic Pressing: $CaZr_{1-x}Ce_xTi_2O_{7.}$ x = 0.1, 0.2, 0.3, 0.4



Can Number	Densification (internal) %
1	43
2	44
3	43
4	42

SEM – HIPed $CaZr_{0.6}Ce_{0.4}Ti_2O_7$





- ZC – zirconolite
- C – cerium
- P – perovskite
- T – rutile
- Z - zirconia

- XRD confirms phase assemblage
- Ceria likely unreacted material
- Perovskite and zirconia could have formed but also possibility of unreacted calcium titanate and zirconium oxide
- Optimisation of pre-processing parameters or possibly higher reaction temperature needed

- Substantial differences in plutonium surrogate behaviour has been identified
- Traditional sintering in oxidising atmosphere leads to pronounced changes in phase assemblage
- The propensity of cerium to reduce leads to formation of secondary phases, highly undesirable for plutonium immobilisation
- The potential of uranium to form higher oxidation states than applicable for plutonium indicates that its use as a surrogate is highly dependent on processing atmosphere
- The refractory nature of ThO_2 in comparison to CeO_2 and UO_2 implies its use as a simulant for PuO_2 is sensitive to processing conditions
- Large cerium oxide inclusions leads to conclusion that optimisation of pre-processing parameters for HIP is needed

The University Of Sheffield.

A WORLD TOP 100 UNIVERSITY

Thank you for listening – any questions?

NucleUS
Immobilisation Science Laboratory

NDA
Nuclear Decommissioning Authority

midas

NATIONAL NUCLEAR LABORATORY