DISTINCTIVE

Studies of the ceramic products from HIPing spent IONSIV

George Day

Introduction

- The removal of both radioactive Cs and Sr from waste streams and storage ponds has become a familiar one in the nuclear industry for the last 40 years.

- Inorganic ion exchangers have found extensive employment in this process due to their excellent properties such as:
  - High selectivity
  - Radiation resistance
  - Effectiveness in wide pH range

- Spent material immobilisation and consolidation for final disposal is an important process:
  - Currently the accepted method is encapsulating into cement [1]
  - Here we propose Hot isostatic pressing or HIPing

1. A. Jenni, N.C. Hyatt, Encapsulation of caesium-loaded Ionsiv in cement, Cement and Concrete Research, 40, 8, 2010, 1271-1277

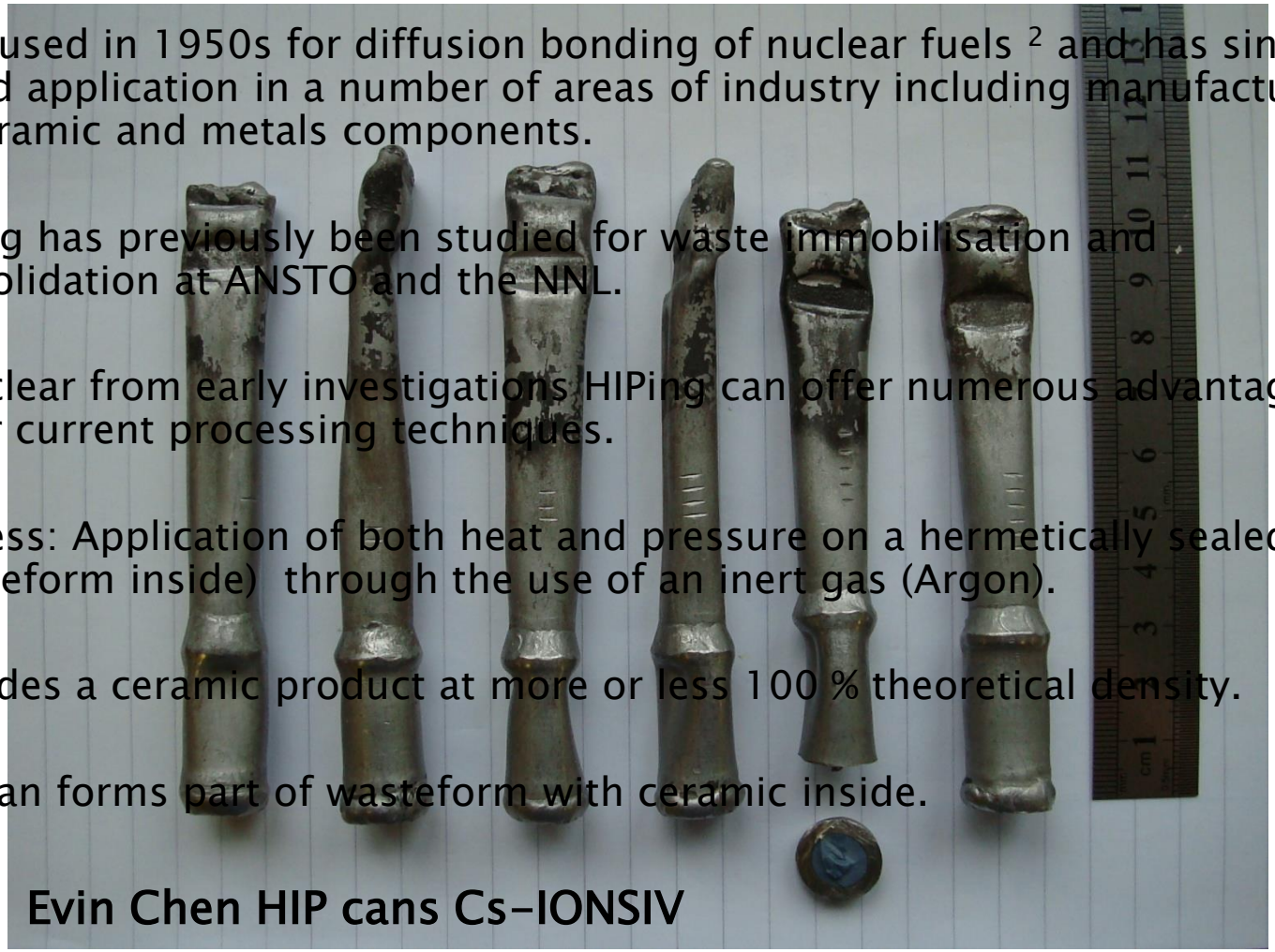
In this study…

- In this study we consider IONSIV IE-911, a commercial exchanger, developed and engineered by UOP (formerly known as Universal Oil Products).

- IONSIV has already demonstrated its utility finding use in the UK, US and also relatively recently at the Fukushima power plant after the disaster in 2011.

Hot Isostatic Pressing (HIPing)

- First used in 1950s for diffusion bonding of nuclear fuels [2] and has since found application in a number of areas of industry including manufacturing of ceramic and metals components.
- HIPing has previously been studied for waste immobilisation and consolidation at ANSTO and the NNL.
- It is clear from early investigations HIPing can offer numerous advantages to other current processing techniques.
- Process: Application of both heat and pressure on a hermetically sealed can (wasteform inside) through the use of an inert gas (Argon).
- Provides a ceramic product at more or less 100 % theoretical density.
- HIP can forms part of wasteform with ceramic inside.



Evin Chen HIP cans Cs-IONSIV

2. M. H. Bocanegra-Bernal, *Journal of Materials Science, 2004, **39, 6399-6420.***

IONSIV IE-911

- Crystalline silicotitinates (CST), with an ideal formula of $Na_2Ti_2O_3(SiO_4)\cdot 2H_2O$.
- CST's consist of a zeolite open framework.
- Substituting some of the Ti^{IV} for Nb^{V} enhances the exchange properties.
- Nb-CST's were further engineered to improve mechanical properties by UOP, binding the active ingredient CST, and $Zr(OH)_4$ giving IONSIV IE-911.
- IONSIV is selective for both Cs and Sr but has mostly been employed for Cs clean up.

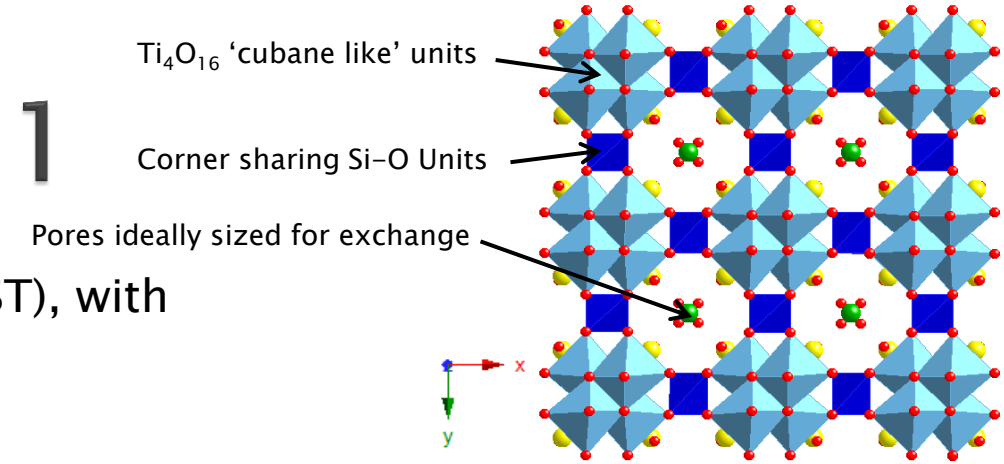


Fig. 1 Crystal Structure of CST, view down the z axis CIF file adapted from Thorogood et al [3]

Fig. 2 IONSIV IE-911

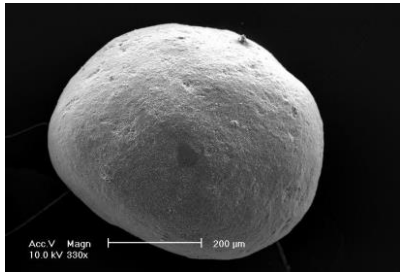


Fig. 3 IONSIV IE-911, SEM, taken by Tzu-Yu Chen [4]

3. G. J. Thorogood, B. J. Kennedy, C. S. Griffith, M. M. Elcombe, M. Avdeev, J. V. Hanna, S. K. Thorogood, and V. Luca, *Chem. Mater.*, 2010, **22**, 4222-4231.
4. T.-Y. Chen, J. A. Hriljac, A. S. Gandy, M. C. Stennett, N. C. Hyatt and E. R. Maddrell, *Scientific Basis for Nuclear Waste Management XXXVI*, *MRS Symp. Proc.* 2013, **1518**, 67-72.

Previous group work

- Evin Chen (PhD, 2012)[4].
- HIPing Cs-loaded IONSIV yields a robust immobilised wasteform suitable for final disposal (Geological disposal facilities, GDF's).
- HIP conditions:
  - 1100 ºC, 190 MPa, Ar atmosphere
- Mild Steel HIP can selected on the basis that little HIP can and wasteform interaction is expected.

4. T.-Y. Chen, J. A. Hriljac, A. S. Gandy, M. C. Stennett, N. C. Hyatt and E. R. Maddrell, *Scientific Basis for Nuclear Waste Management XXXVI*, *MRS Symp. Proc.* 2013, **1518**, 67-72.

Phase assemblage of HIPed Cs-IONSIV

Table 1. Phases produced from HIPing Cs – IONSIV, Rietveld weight fraction analysis

Phase	4wt	6wt	8wt	10wt	12wt
$Cs_2TiNb_6O_{18}$	17.56	26.07	25.65	28.39	24.56
$Cs_2ZrSi_6O_{15}$	0	0	18.65	19.42	31.26
$ZrSiO_4$	12	3.55	0	0	0
$ZrTiO_4$	37.64	41.54	34.66	29.4	19.91
SiO_2	7.05	0	0	0	0
$(Ti,Nb)O_2$	27.54	28.85	21.04	22.79	24.27

- Weight % calculated using [Cs(g) / Cs (g) + IONSIV (g)] x 100
- Two major Cs phases:
  - At lower Cs levels mainly $Cs_2TiNb_6O_{18}$
  - $Cs_2ZrSi_6O_{15}$ begins to grow in at higher Cs levels
- $Cs_2TiNb_6O_{18}$ and $Cs_2ZrSi_6O_{15}$ both demonstrated to be excellent Cs wasteforms, particularly $Cs_2TiNb_6O_{18}$ with comparable properties to hollandite (main Cs ceramic phase in SYNROC).
- No real concern with HIP can and sample interaction.

Continued…

- HIPed Cs IONSIV samples demonstrated excellent leach rates.
- Leach rates from HIPing Cs IONSIV very low and compare well to previously reported Cs wasteforms:
  - Hollandite rich SYNROC wasteform: 0.62 – 2.8 $g \cdot m^2 \cdot day^{-1}$
- Therefore can conclude that the materials produced from Cs-IONSIV HIPing have great potential as a final wasteform.

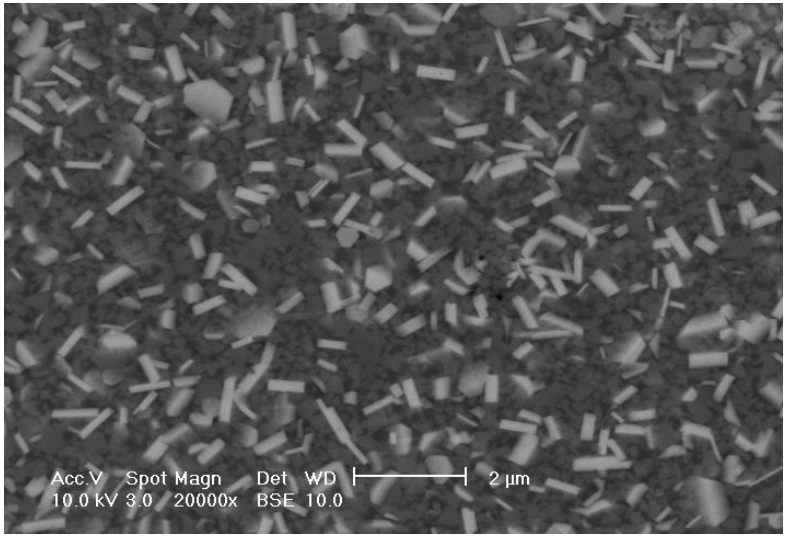


Fig. 4 SEM BSE 8 wt% Cs – IONSIV taken by Tzu – Yu Chen

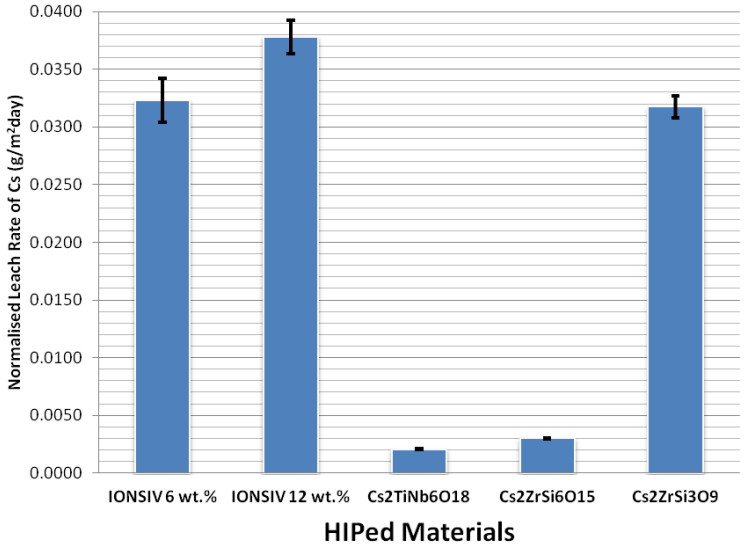


Fig. 5 Leach Tests (PCT-B, 7 days) taken by Tzu-Yu Chen

Sr – IONSIV HIPing

- Considering the success of Cs-IONSIV HIPing, products from HIPing Sr-IONSIV also studied.

- Different Sr levels exchanged:
  - Initial targets of 1.5 and 3 wt% Sr exchange
  - $H_2NaTi_{1.4}Nb_{0.6}SiO_7 2.2Zr(OH)_4 \cdot xH_2O + 0.1Sr^{2+} \rightarrow H_2Sr_{0.1}Na_{0.8}Ti_{1.4}Nb_{0.6}SiO_7\ 2.2Zr(OH)_4 \cdot xH_2O + 0.5Na^+$
  - Abbreviates: Na-IONSIV + Sr2+ → (Sr/Na)-IONSIV + Na^+

- Successful exchange was confirmed via X-ray florescence spectroscopy before samples sent for HIPing.

- HIPing at 1100°C, 150 Mpa, Ar atmosphere

X-ray Diffraction

- A number of crystalline phases formed through HIPing
- Phase compositions of both 1.5 and 3 wt % similar from XRD
- Appears Sr resides in a crystalline Sr – Perovskite phase
- Potentially encouraging as Sr perovskite known to be a robust wasteform (A major phase of the SYNROC formation)
- Basic Phase Assembly:
  - $ZrSiO_4$
  - (Ti,NbO_2)
  - $NaNbO_3$
  - (Na,Sr) (Ti,Nb,Zr) O_3 Perovskite
  - Possibly SiO_2, difficult to confirm at this point

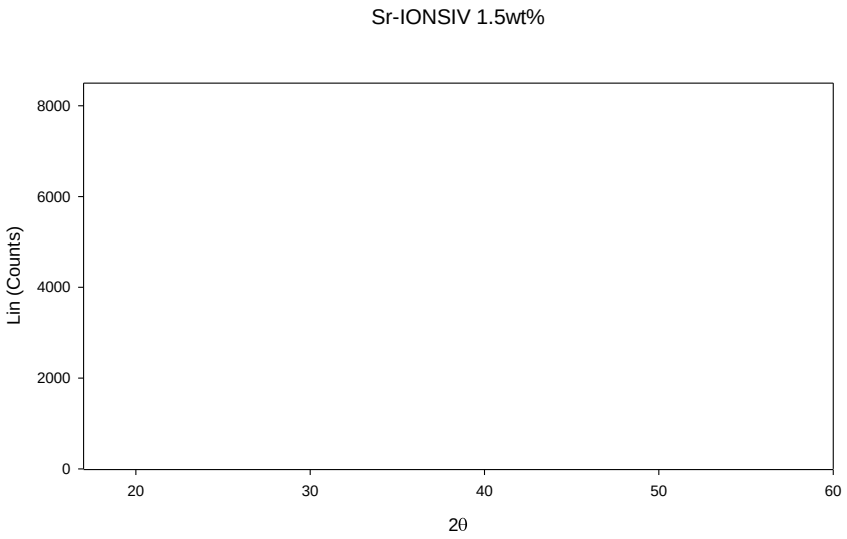


Fig. 6 XRD 1.5 wt % Sr – HIPed IONSIV

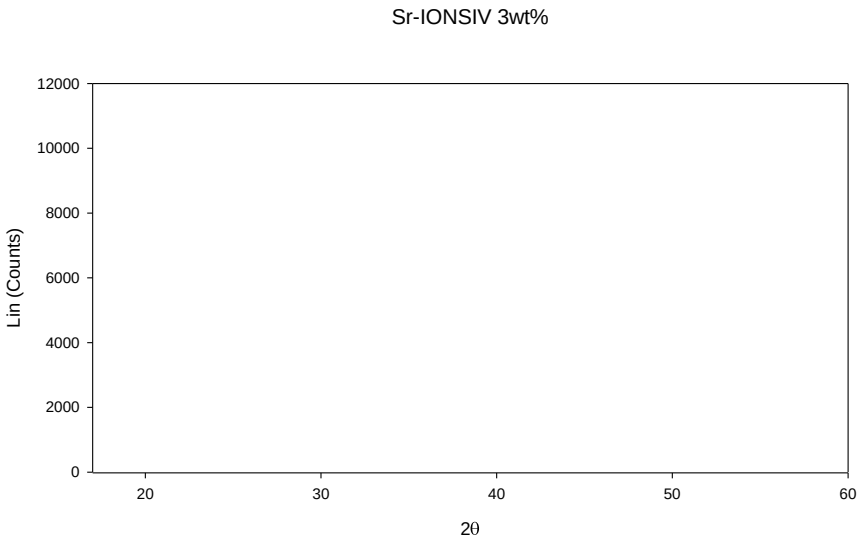


Fig. 7 XRD 3 wt % Sr – HIPed IONSIV

Rietveld – Weight fraction analysis

- In order to try a quantify the phases present Rietveld analysis carried out.
- This process caused a number of issues.
- Some amount of peak overlap of $NaNbO_3$ and Sr perovskite phases.
- Due to the nature of the Sr phases difficult to know the exact elemental composition.
- However initial results suggest:

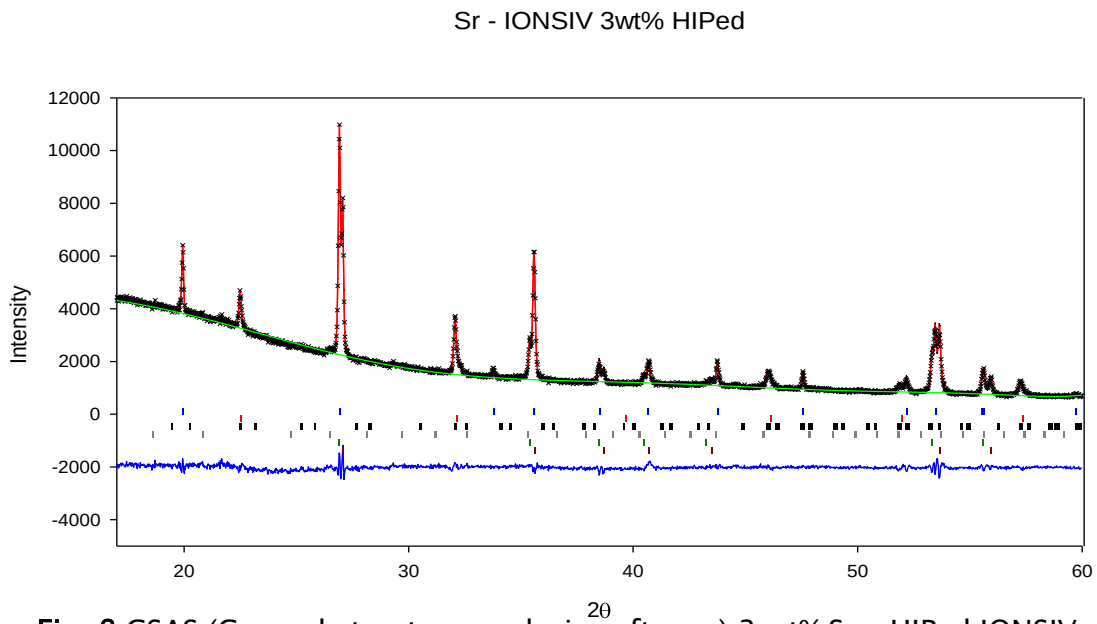
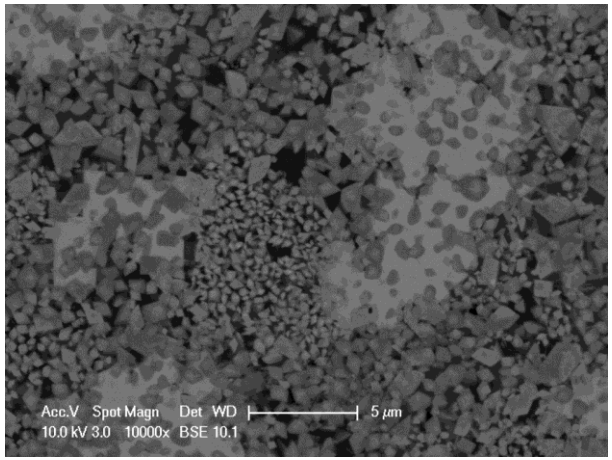


Fig. 8 GSAS (General structure analysis software) 3 wt% Sr – HIPed IONSIV

Table 2. GSAS weight fractions 3 wt %

Phase	Wt/%
$ZrSiO_4$	32.3 (3)
$Sr_{0.5}Na_{0.5}Ti_{0.5}Nb_{0.5}O_3$	7.3(3)
$NaNbO_3$	7.3(2)
$(Ti,Nb)O_2$	53.14

SEM



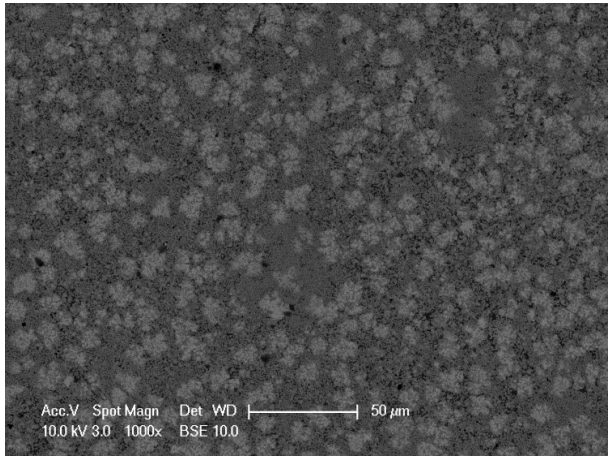
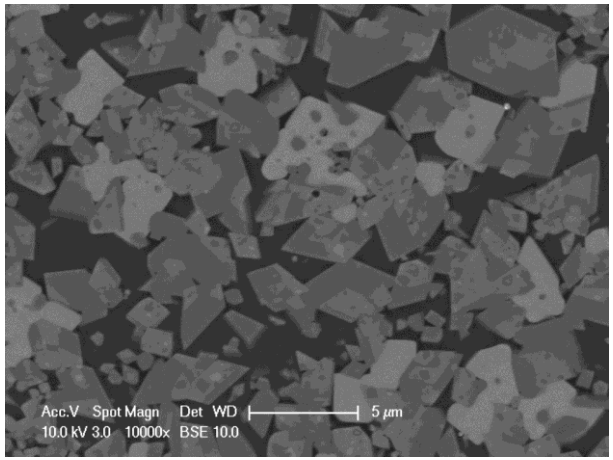


Fig. 9 BSE 3 wt % Sr-IONSIV



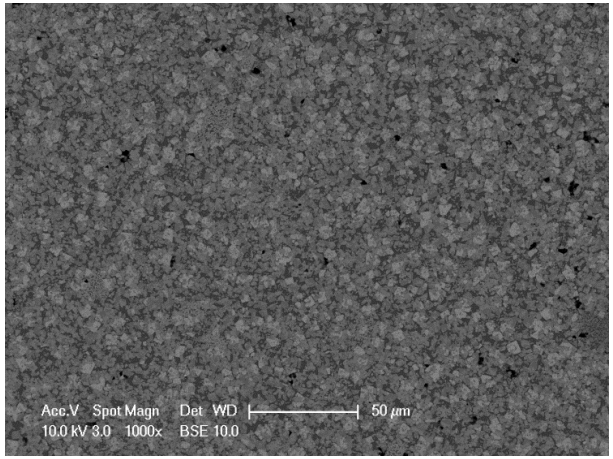


Fig. 10 1.5 wt % Sr-IONSIV

- Different morphologies for both the 1.5 and 3 wt % regions at 50-100 µm
- At higher magnification it becomes clear that at the higher Sr loading, we see smaller grains than the lower Sr loadings
  - This may be a result of more Sr to grow smaller particles
  - Small grains difficult with EDS to identify particular phases although it was possible to detect Sr in both wasteforms

TEM: The search for Sr!

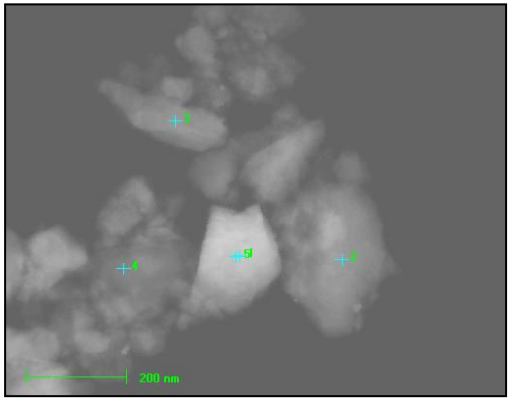


Fig 11. Multi-point analysis TEM

Table 3. EDS analysis

Wt%	C K	O K	CuL	NaK	SiK	TiK	FeK	**SrK**	ZrK	NbK
multipoint1	49.37	9.09	1.03	3.24	1.4	1.17	0.53	**7.27**	1.16	25.74
multipoint2	64.38	9.3	0.89	0	0.39	12.18	2.68	**0.19**	1.41	8.59
multipoint3	63.27	8.74	0.67	0.04	0.31	12.91	2.86	**0.33**	1.75	9.12
multipoint4	62.55	16.72	0.66	0.03	18.94	0.16	0.26	**0.16**	0.25	0.28
multipoint5	60.66	6.88	1.02	2.46	1.09	0.96	0.48	**5.63**	0.8	20.02

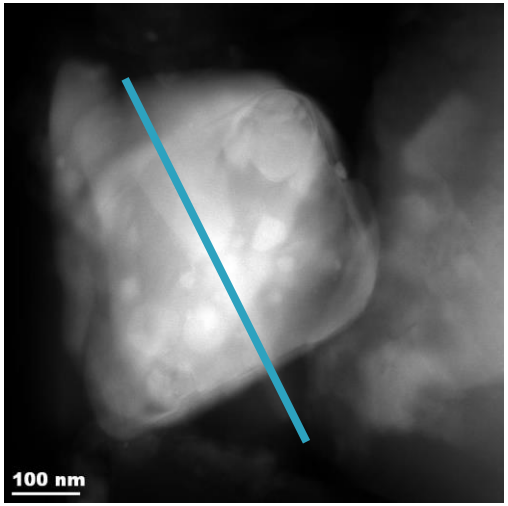


Fig 12. Line analysis TEM

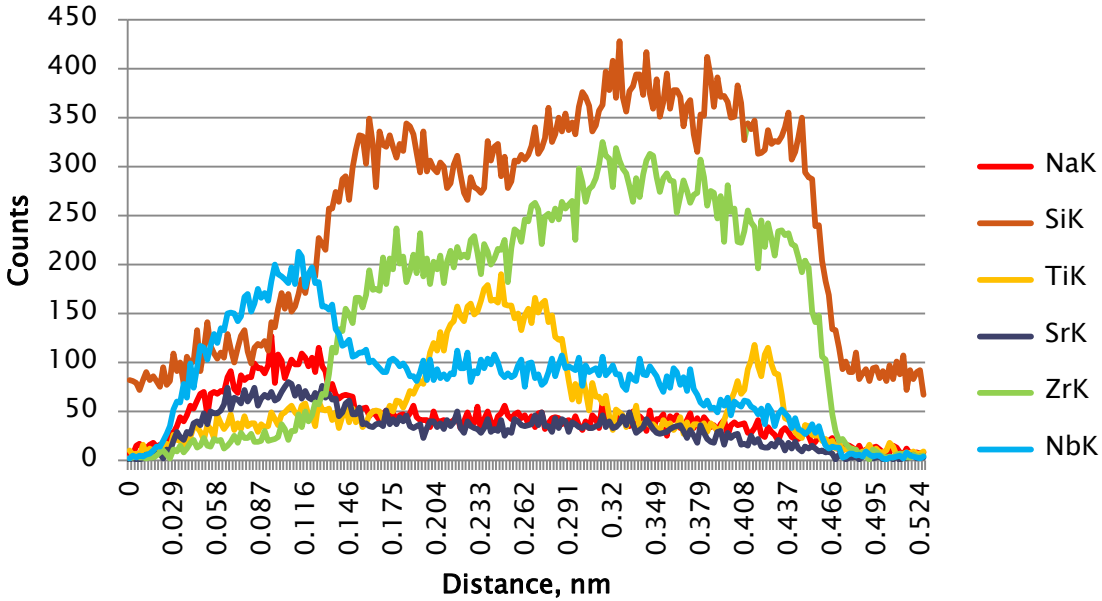


Fig 13. Graph showing concentration of each element versus line distance

TEM

- Examining the boxed area more closely we can see **Sr**, **Na**, **Ti**, **Nb** and possibly **Zr** follow a trend.
- This is likely to be the perovskite phase identified by XRD.
- Difficult to confirm unanimously at this point.

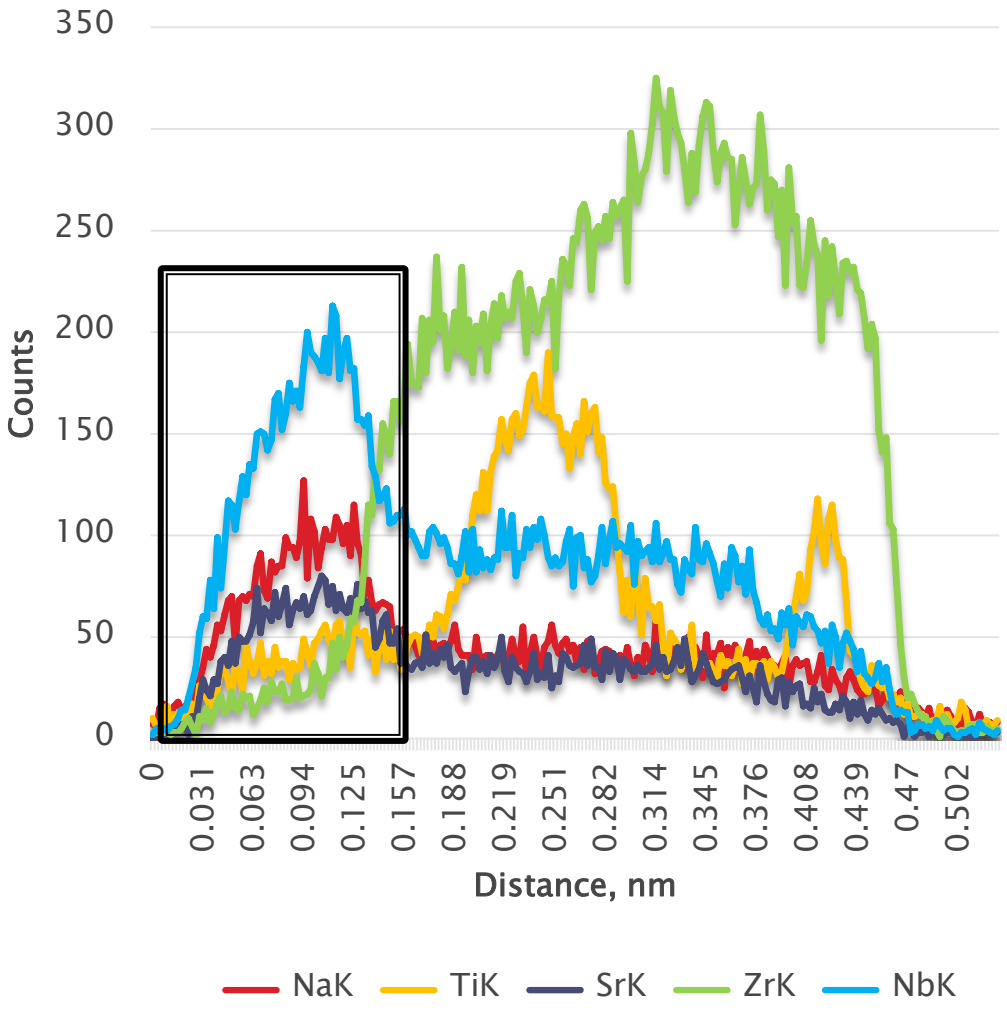


Fig 14. Graph showing concentration of Na, Ti, Sr, Zr and Nb.

TEM Continued. The search for Sr is still on

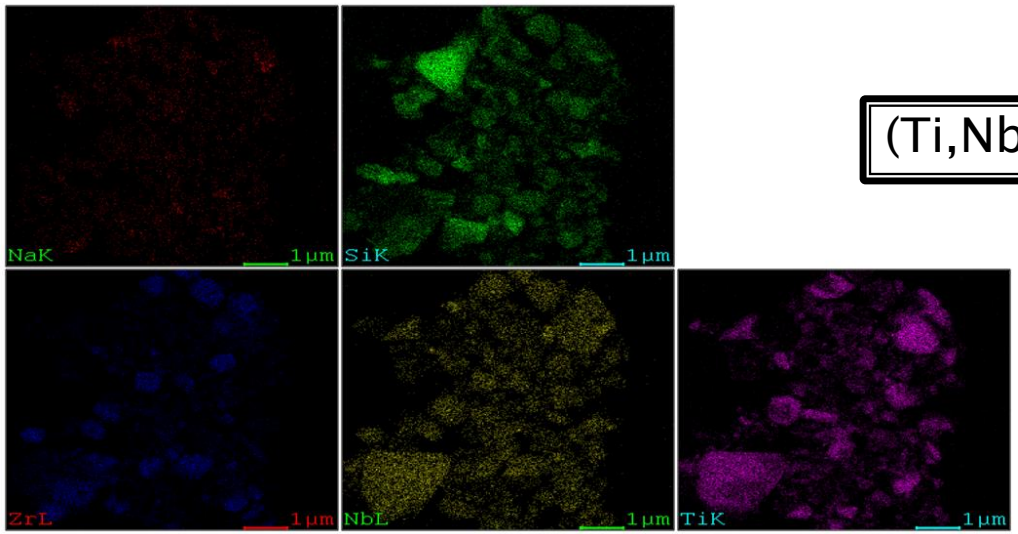


Fig. 15 Elemental mapping, Na K, Si k, Zr L, Nb L and Ti K

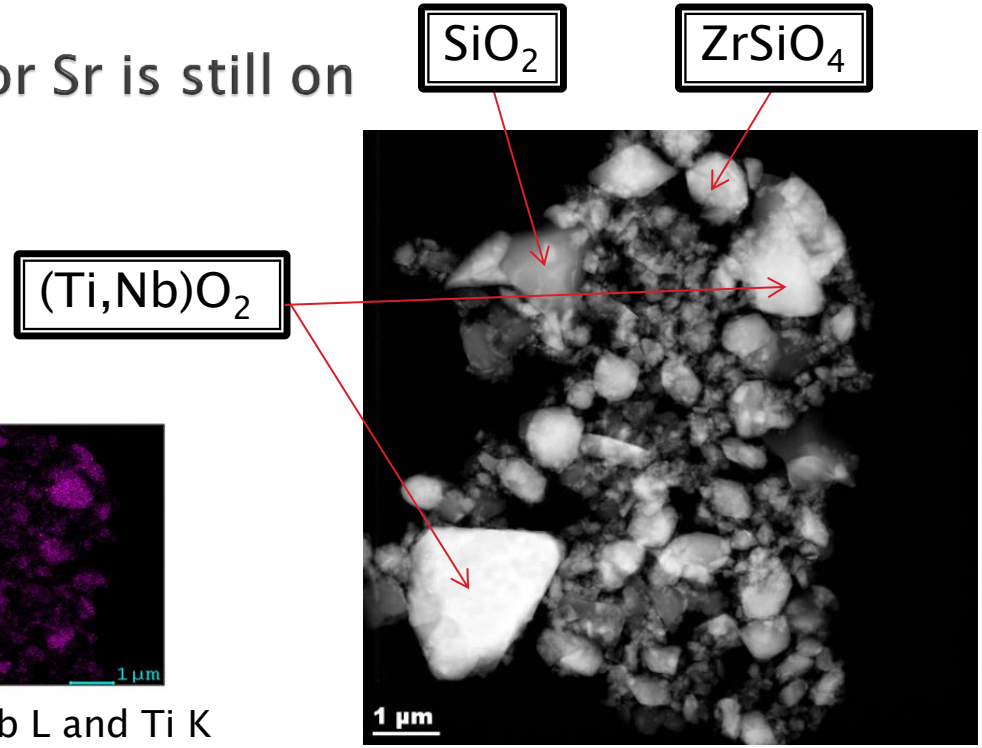


Fig. 16 TEM, SE 3 wt % IONSIV

- It is evident from elemental mapping (figure 15) that some of the phases expected from XRD are present
- Cleary from mapping and figure 16 we can see SiO_2, $ZrSiO_4$ and $(Ti,Nb)O_2$ phases are present
- There seems to be a wide distribution of the Na which from line analysis we could expect Sr to reside with in a 'perovskite like' phase
- Sr could not be mapped due to it being present in such low concentrations, therefore it was difficult to assign a specific Sr phase

Further work

- Further analysis of TEM work
- MCC-1 Leach testing to ultimately assess the wasteform
- Synchrotron XRD data to attempt to better quantify the weight fractions and in particular the exact composition any Sr phases
- Further analysis of HIPed Sr – IONSIV at higher Sr dopings, may elude more durable Sr phases, especially for Sr elemental mapping

Other work…

- $Cs_2TiNb_6O_{18}$, durable phase produced from HIPing
- Pyrochlore analogue, not previously studied for wasteform applications before despite having excellent potential as a final Cs wasteform
- Ba doping studies carried out in order to test if $Cs_2TiNb_6O_{18}$ can retain the transmutation products of ^{137}Cs
- A number of Ba- doped samples synthesised and characterised using XRD, XRF, SEM and TEM.
- Computational studies also carried out in order to assess the stability of Ba doped $Cs_2TiNb_6O_{18}$ systems.
  - Novel Potentials derived for numerous phases

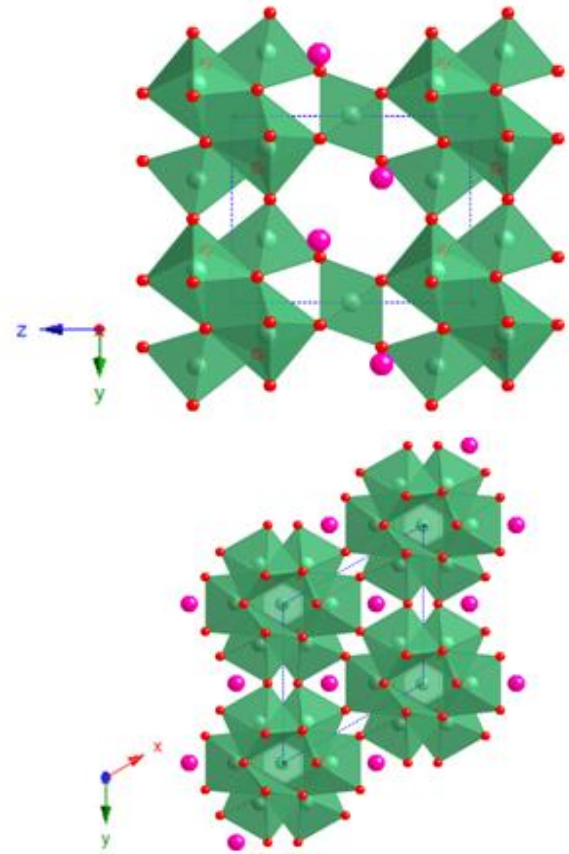


Fig. 17 Crystal Structure of $Cs_2TiNb_6O_{18}$. Sourced from Desgardin et al [5]. Top: view down a axis. Below: view down c axis

5. G. Desgardin, C. Robert, D. Groult, and B. Raveau, *J. Solid State Chem.*, 1977, **22**, 101–111.

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Thank you for listening!

Questions?