Novel Ion Exchange Materials

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Background

Experimental	**Computational**
Dr Evin Chen	Dr Paul Martin
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- The main aim of this project is to develop new materials for effluent clean-up, especially for Sr and Cs under “non-standard” conditions such as acidic solutions or the presence of complexants from decontamination processes.
- The strategy is to make synthetic forms of minerals that look suitable for ion exchange, e.g. with hydrated cations (Na, K) loosely bound. Atomistic modelling is being developed on known systems so that in the future computational screening can be used before synthesis/testing.

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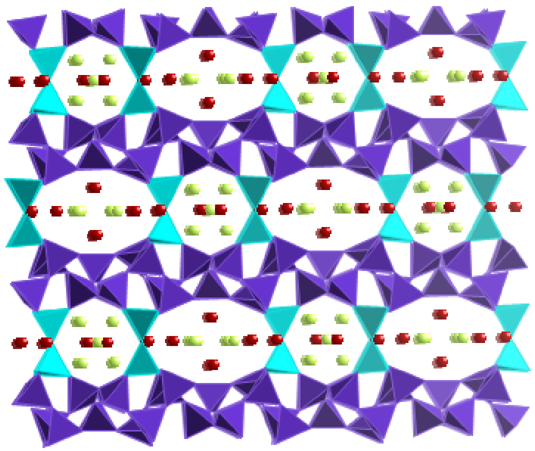
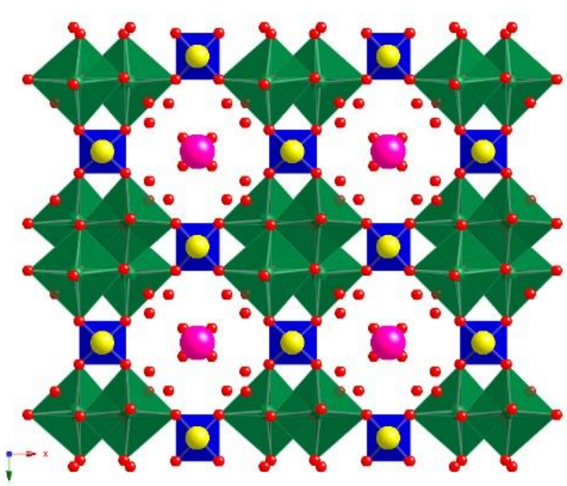
Current Systems – Cs and Sr



- Zeolite Clinoptilolite
- $(Na,K,Ca)_3Al_3Si_{15}O_{36}{\sim}10H_2O$
- Supply from Mud Hills (USA) used in SIXEP (variability in ion exchange ability with source)
- Ion exchange properties pH dependent
- Dissolution of Si and Al from the framework
- Current disposal route is cementation



- Nb-CST: $Na_{1.5}Ti_{1.5}Nb_{0.5}O_3SiO_4{\cdot}2H_2O$ as found in IONSIV
- Better Cs^+ affinity achieved by partially substituting Ti^{4+} with **Nb^{5+}.**
- Reduce the amount of Na^+ required for charge neutralisation and facilitate more Cs into the less crowded tunnels.
- Works in a wide pH range.
- Expensive, poor handling properties, disposal route?

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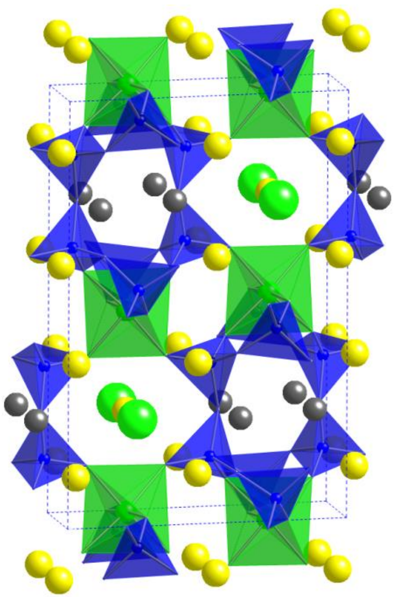
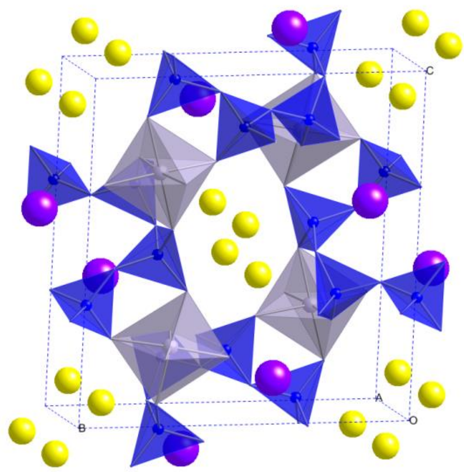
Target Materials

- Starting points are various M^{IV} silicates (M = Ti, Zr, Sn) based on known, stable minerals. Some of these have already been studied by S Savva under the NDA bursary scheme.

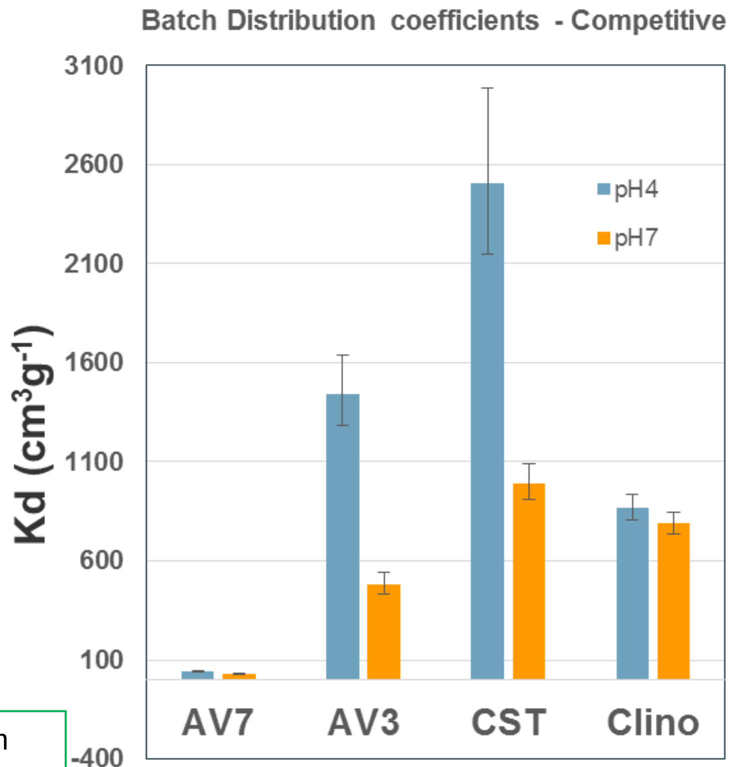


Petarasite (AV-3)
$Na_5Zr_2Si_6O_{18}(Cl,OH)\cdot 2H_2O$



Sn-Kostylevite (AV-7)
$Na_{0.5}K_{1.5}SnSi_3O_9\cdot H_2O$

Sr exchange tests



Distribution coefficients (K_d)

$$K_d = \frac{(A_i - A_t)}{A_t} \times \frac{V}{m} \quad (cm^3/g)$$

where Ai and At are, respectively, the initial and equilibrium activities of the radionuclide
V the volume of solution and m(g) the weight of zeolite

Na^+ 100 ppm
K^+ 10 ppm
Mg^{2+} 20 ppm
Ca^{2+} 20 ppm
Cs^+ 10 ppm
Sr^{2+} 10 ppm
$^{85}Sr^{2+}$ 450 kBq

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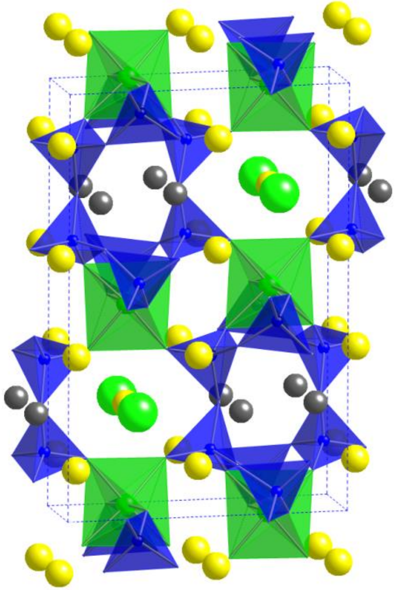
Zirconium silicate

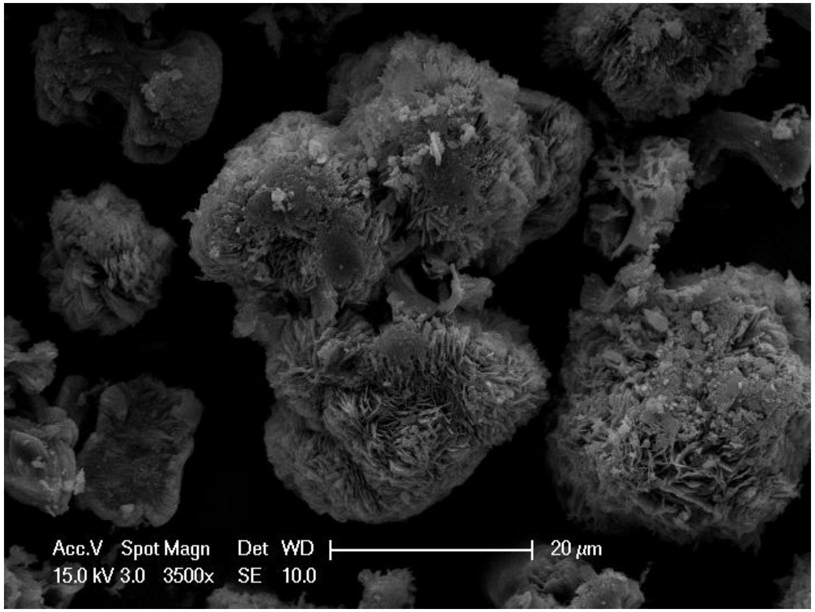


Petarasite(AV-3)

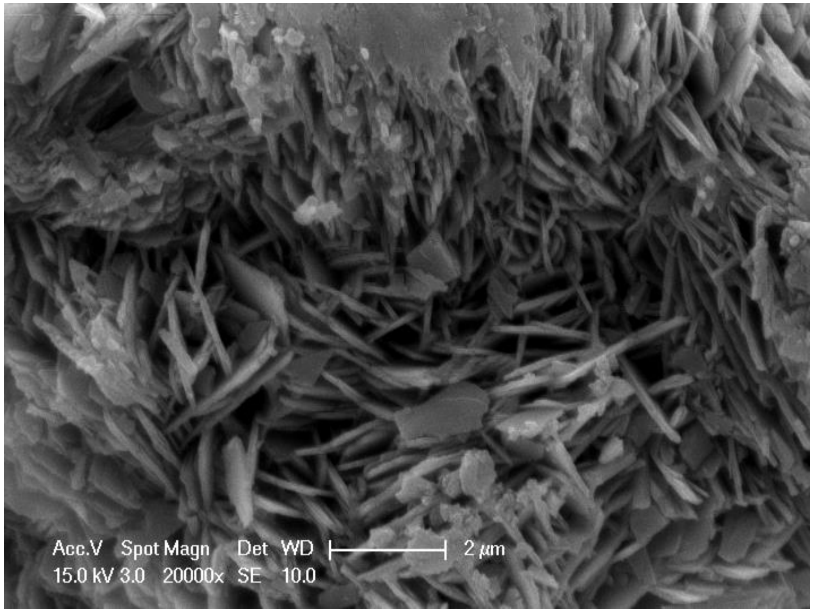
$Na_5Zr_2Si_6O_{18}(Cl,OH)\cdot 2H_2O$

Monoclinic, $P2_1/m$
a= 10.771,
b = 14.505,
c = 6.575 Å
β = 13.214°

~20 μm



Sheet-like



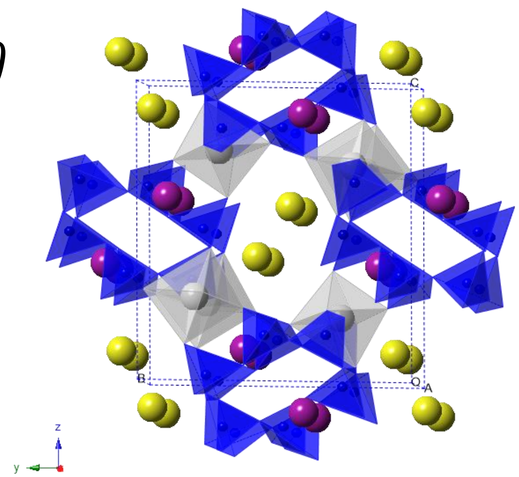
Tin silicates

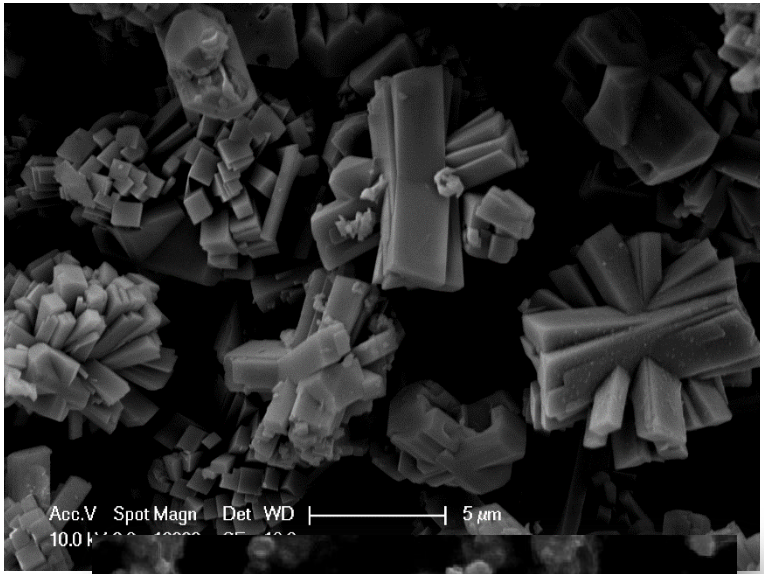
Chemically and thermally stable materials

Sn-Kostylevite *(AV-7)*

$(Na,K)_2SnSi_3O_9 \cdot H_2O$
Monoclinic, $P2_1/n$
$a = 6.554$,
$b = 11.763$,
$c = 13.028$ Å,
$\beta = 103.57^{\circ}$

- **cyclohexasilicate**

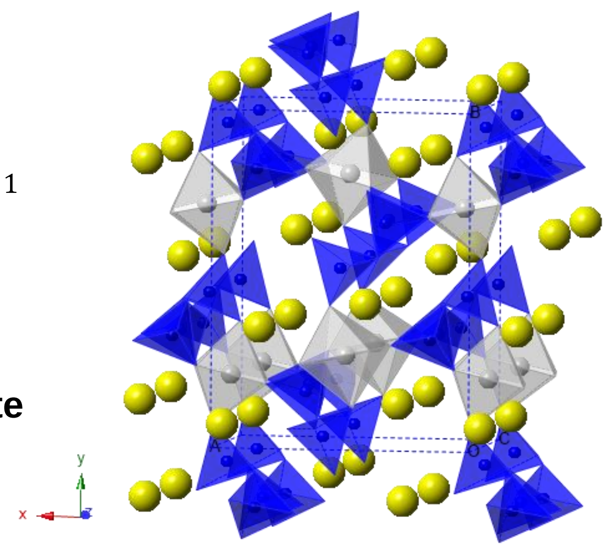


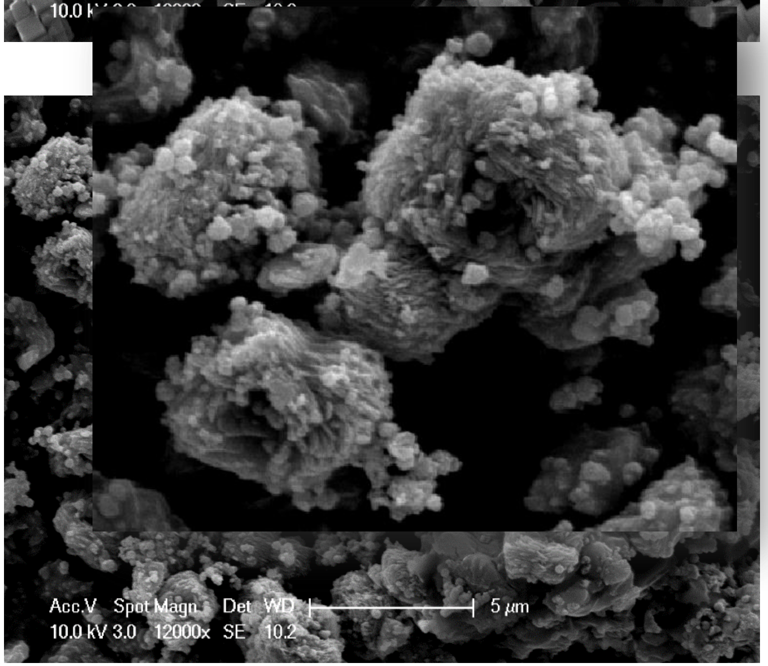


Sn-Umbite *(AV-6)*

$K_2SnSi_3O_9 \cdot H_2O$
Orthorhombic, $P2_12_12_1$
$a = 10.085$,
$b = 13.110$,
$c = 7.159$ Å

- **long-chain polysilicate**





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Ion exchange

0.1 M $Sr(NO_3)_2$ V/m=100 mL/g
Shake for 24 hrs
XRF analysis on loose powder

Table 1 Sr uptake in K-Sn-umbite

	Before		**After**	
	wt.%	**at. (to Si)**	**wt.%**	**at. (to Si)**
Sn	23.20%	0.52	19.59%	0.54
K	15.10%	1.04	12.08%	1.01
Si	10.48%	1	8.63%	1
Sr	-	-	**2.64%**	**0.10**

Table 2 Sr uptake in (Na,K)-Sn-kostylevite

	Before		**After**	
	wt.%	**at. (to Si)**	**wt.%**	**at. (to Si)**
Sn	34.24%	0.57	22.32%	0.46
K	14.45%	0.73	13.19%	0.82
Si	14.15%	1	11.57%	1
Na	2.79%	0.24	1.54%	0.16
Sr	-	-	**2.90%**	**0.08**

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Ion exchange

0.1 M $Sr(NO_3)_2$ V/m=100 mL/g
Shake for 24 hrs
XRF analysis on loose powder

Sr uptake in **Clino(NNL)**

	Before		After	
	wt%.	at. (to Si)	wt%.	at. (to Si)
Sr	1.16%	0.023	**15.85%**	**0.697**
Si	25.12%	1	11.08%	1
Al	4.08%	0.169	3.93%	0.369
Ca	2.04%	0.057	1.70%	0.108
K	1.66%	0.047	1.49%	0.097
Na	1.14%	0.055	0.25%	0.028
Fe	1.01%	0.020	1.03%	0.047
Ba	0.41%	0.003	0.42%	0.008
Mg	0.24%	0.011	0.19%	0.020
P	0.14%	0.005	0.13%	0.011
Ti	0.11%	0.003	0.10%	0.005

Sr uptake in **Clino(zeoclere)**

	Before		After	
	wt%.	at. (to Si)	wt%.	at. (to Si)
Sr	0.27%	0.005	**7.05%**	**0.143**
Si	25.43%	1	24.09%	1
Al	4.20%	0.172	3.82%	0.165
K	3.29%	0.093	3.28%	0.098
Fe	**1.21%**	**0.024**	**1.34%**	**0.028**
Ca	1.18%	0.033	1.10%	0.032
Na	0.56%	0.027	0.32%	0.016
Mg	0.30%	0.014	0.20%	0.010

variability in ion exchange ability with source

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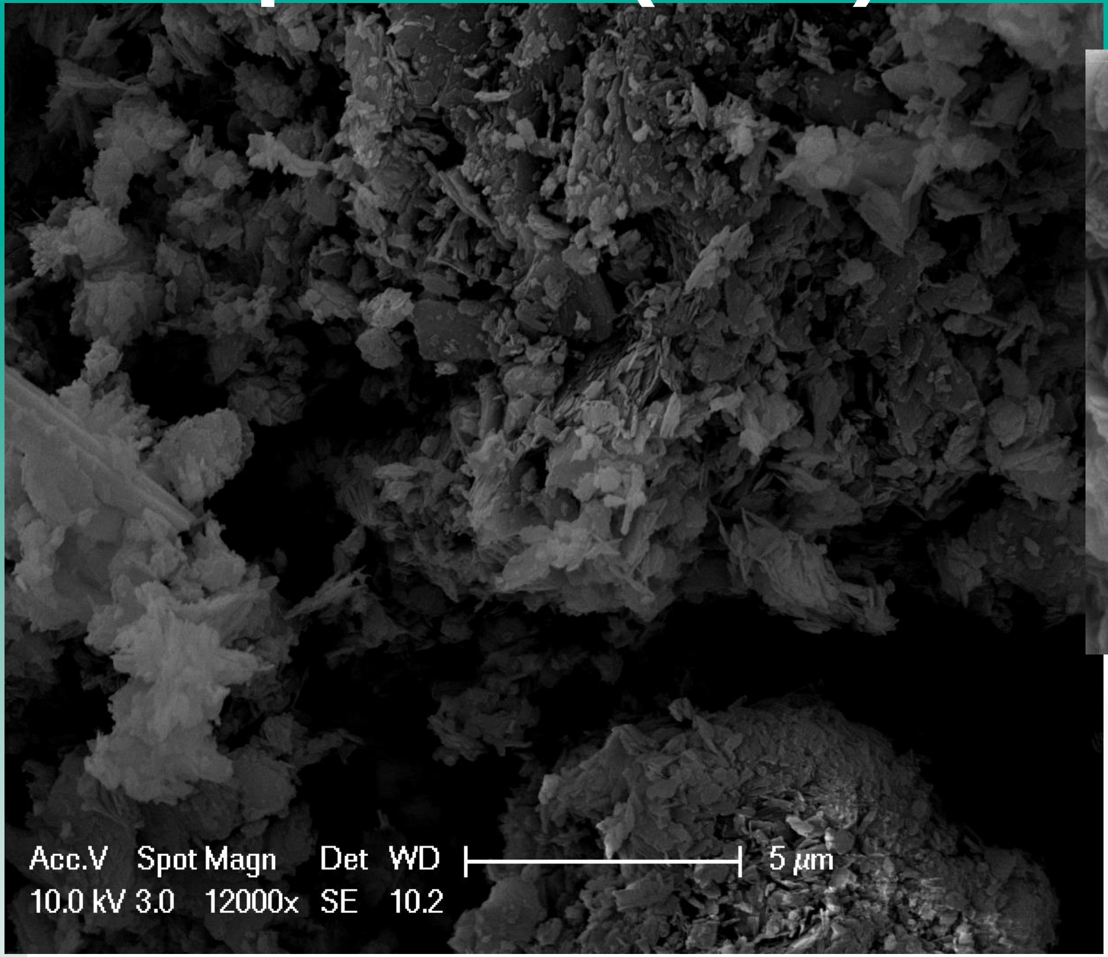
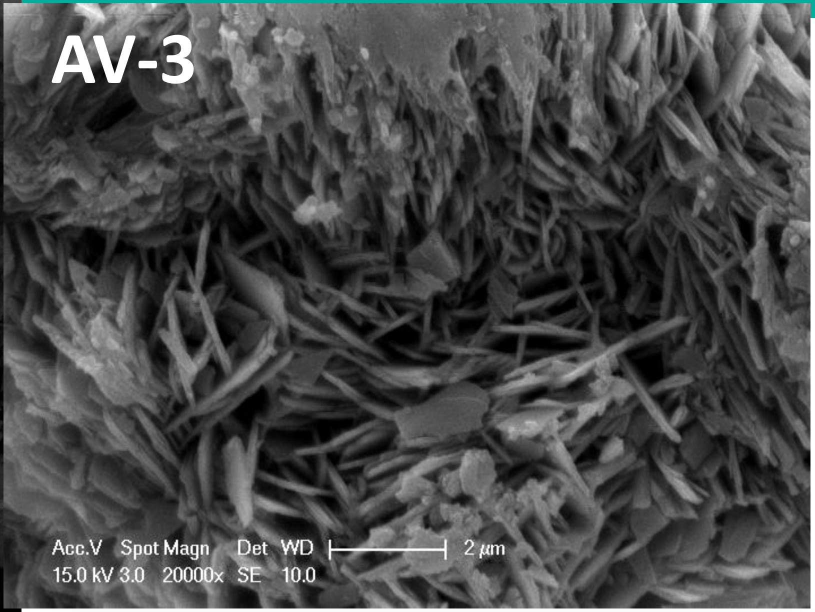
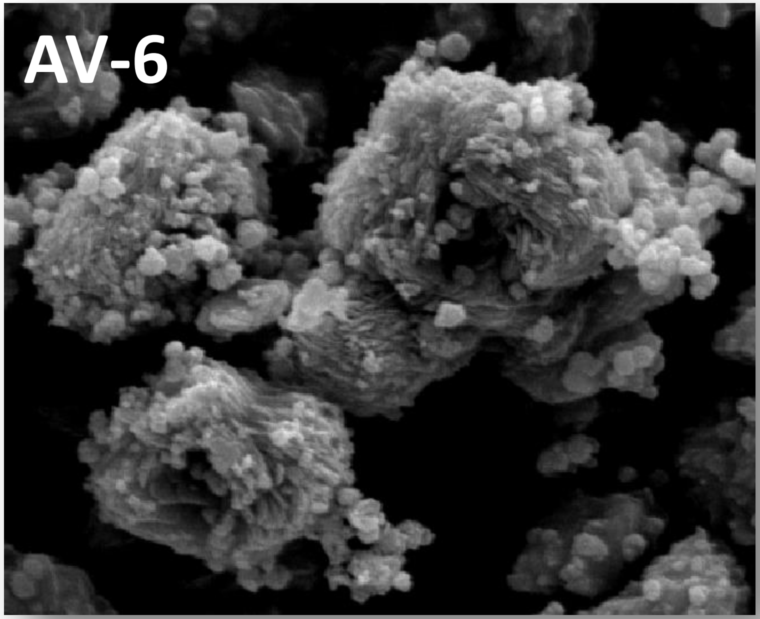
Clinoptilolite (NNL)







Exchange rate maybe influenced by?

- **Sheet microstructure**
- **High surface area**

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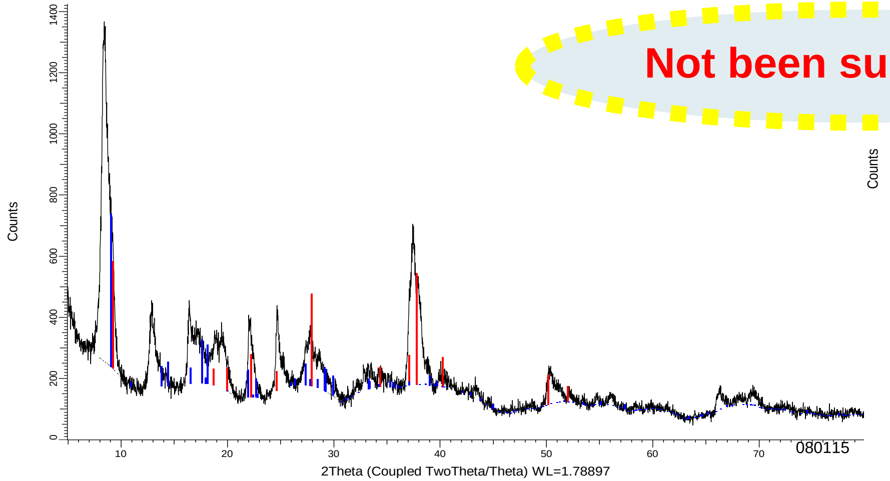
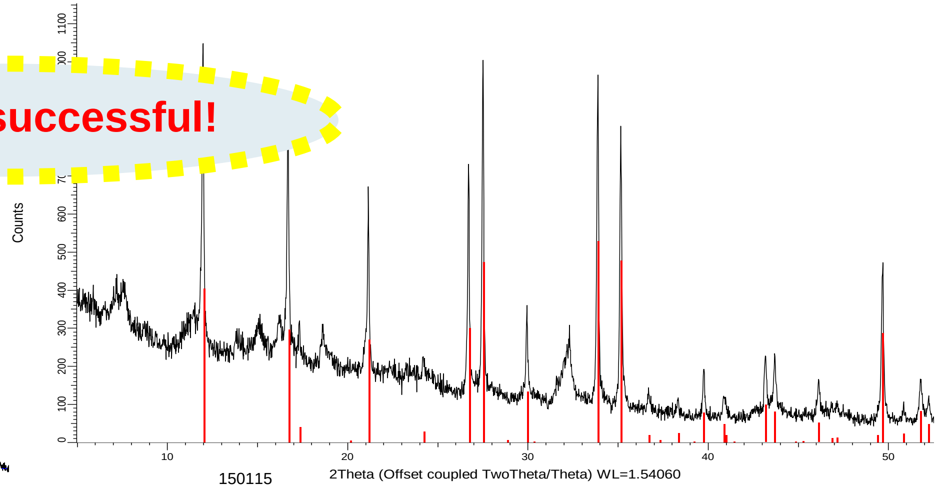
Na-form Tin silicates – direct synthesis

Target:Na_2**Sn**Si_3O_9·**2**H_2O (AV-10)
(Ferrira et al. 2001)
Product: $Na_4\ Sn\ Si_5\ O_{14}\cdot xH_2O$
Impurity: Silicon oxide

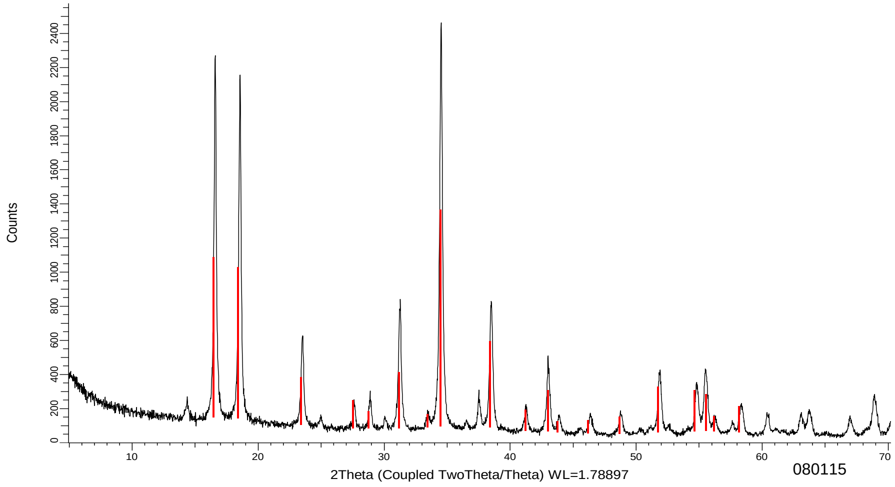


Target:Na_2**Sn**Si_3O_9·**2**H_2O (AV-10)
(Ferrira et al. 2001) Higher pressure, longer heat treatment
Product: $Na_8\ Sn\ Si_6\ O_{18}$
Impurity: SnO, SiO_2

Not been successful!



Target:Na_2**Sn**Si_3O_9·**2**H_2O (Na-umbite)
(Navascu´es et al. 2008)
Product : $Na_4\ Sn\ Si_4\ O_{12}\cdot xH_2O$
Impurity: SnO, SiO_2



Na-form Tin silicates – ion exchange

Ion exchange with 2 M NaCl(aq) for 24 hrs

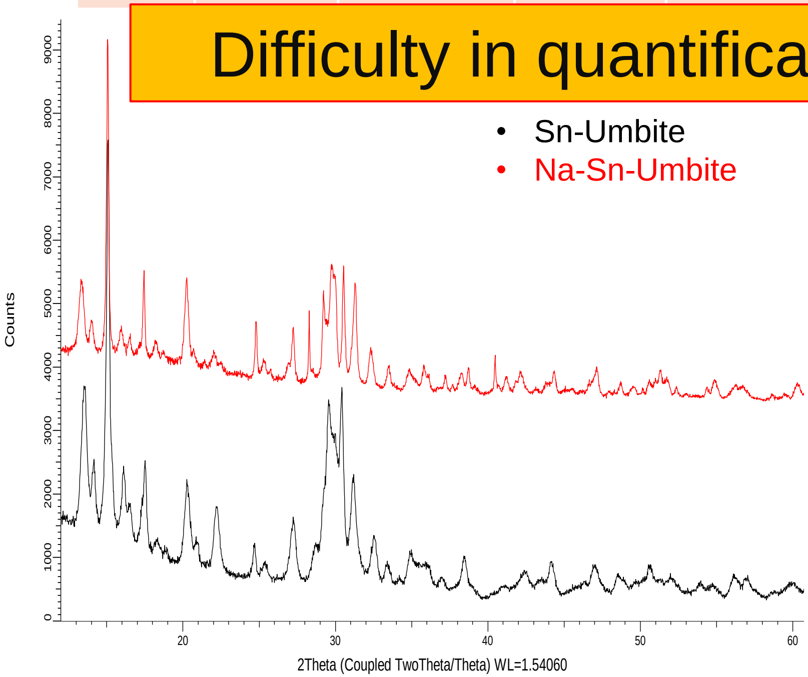
K-Sn-Umbite

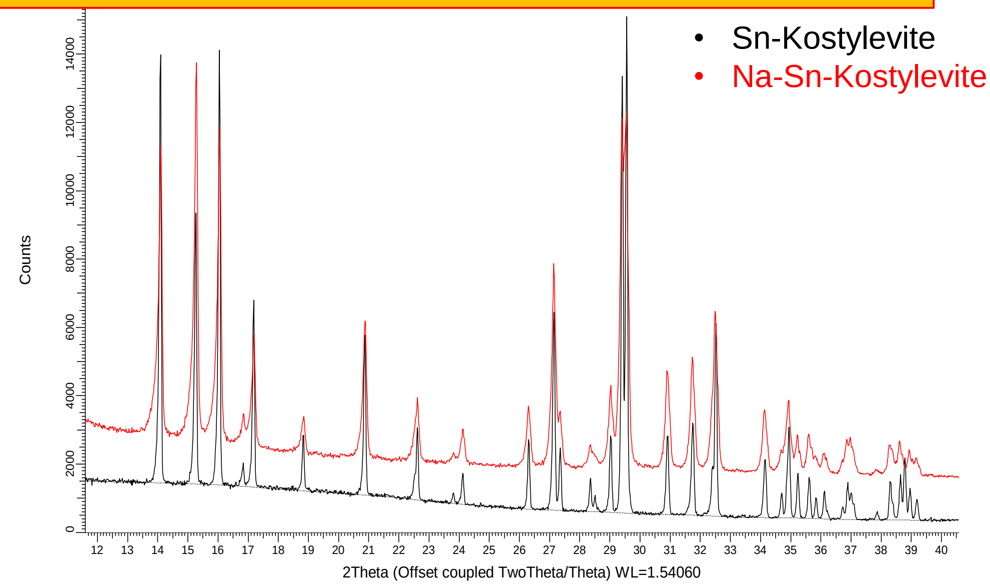
	Before		After	
	wt.%.	at. (to Sn)	wt.%	at. (to Sn)
Sn	23.20%	1	43.07%	1
Si	15.10%	1.98	7.51%	0.53
K	10.48%	**2**	8.78%	**0.86**
Na			**6.20%**	**0.74**

(Na,K)-Sn-Kostylevite

	Before		After	
	wt.%	at. (to Sn)	wt.%	at. (to Sn)
Sn	34.24%	1	24.50%	1
K	14.45%	**1.28**	13.74%	**1.71**
Si	14.15%	1.75	11.72%	2.03
Na	2.79%	**0.42**	1.95%	**0.41**

Difficulty in quantification using XRF and refinement





H-form Tin silicates

Advantages:

- The exchange process is often **accelerated** when using a H-form ion exchanger.
- A protonated material will serve to **decrease the pH** of the overall solution when it is performed in caustic solution.
- Powder XRD patterns will be more sensitive to ion exchange than for the parent material due to the insignificant contribution of H to the total scattering. This will facilitate understanding of the exchange process to be backed up with atomistic modelling.

H-form materials were made via ion exchange with 0.1 M acetic acid for 1 day.

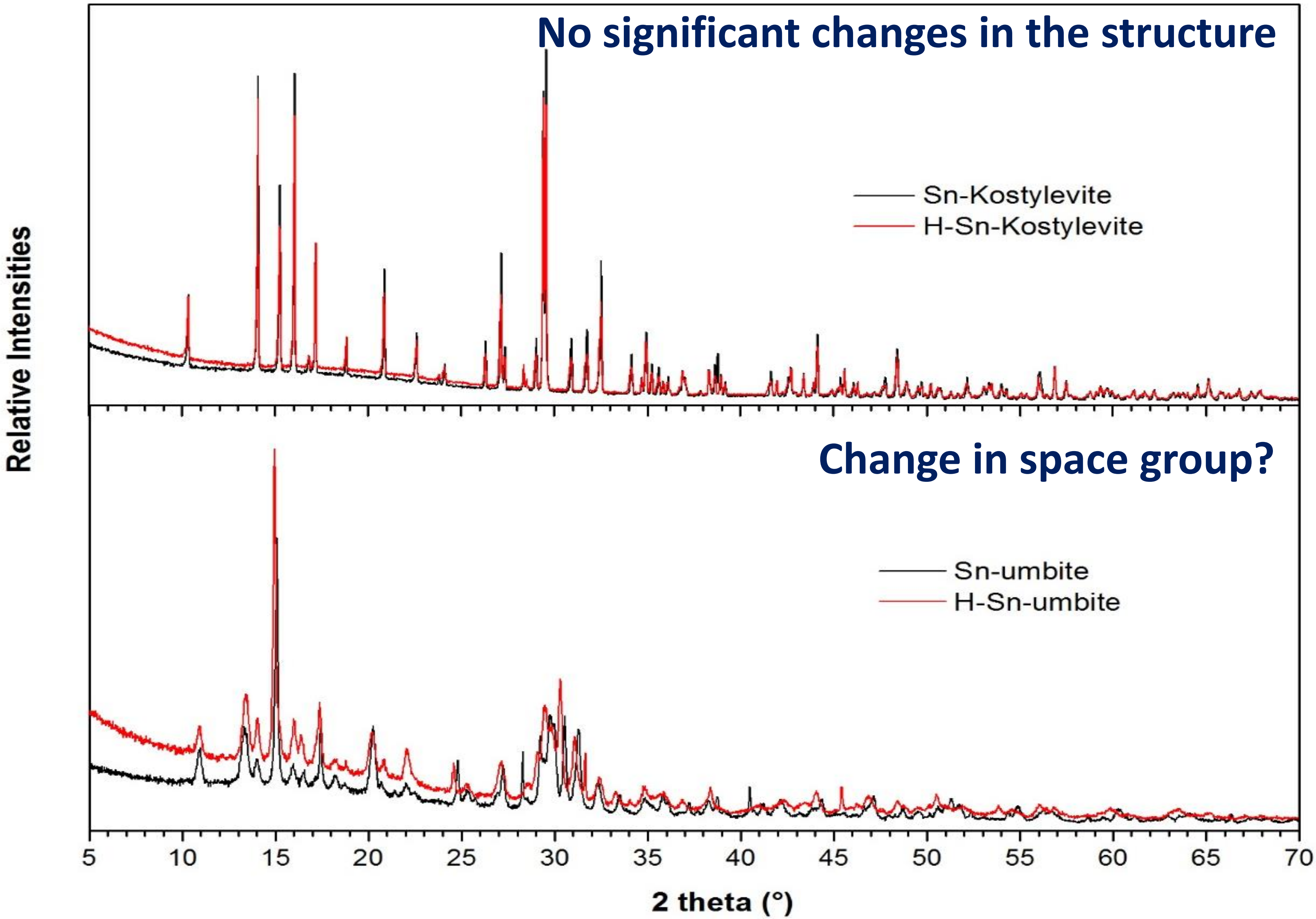
H (acetic acid)-exchanged K-Sn-Umbite

	Before		After	
	wt.%.	at. (to Sn)	wt.%	at. (to Sn)
Sn	23.20%	1	20.65%	1
Si	15.10%	1.98	5.78%	0.85
K	**10.48%**	**2**	**5.85%**	**1.20**

H (acetic acid)-exchanged (Na,K)-Sn-Kostylevite

	Before		After	
	wt.%	at. (to Sn)	wt.%	at. (to Sn)
Sn	34.24%	1	19.71%	1
K	**14.45%**	**1.28**	**7.11%**	**1.10**
Si	14.15%	1.75	8.86%	1.90
Na	**2.79%**	**0.42**	**0.71%**	**0.19**

Tin silicates ion exchanged with acetic acid

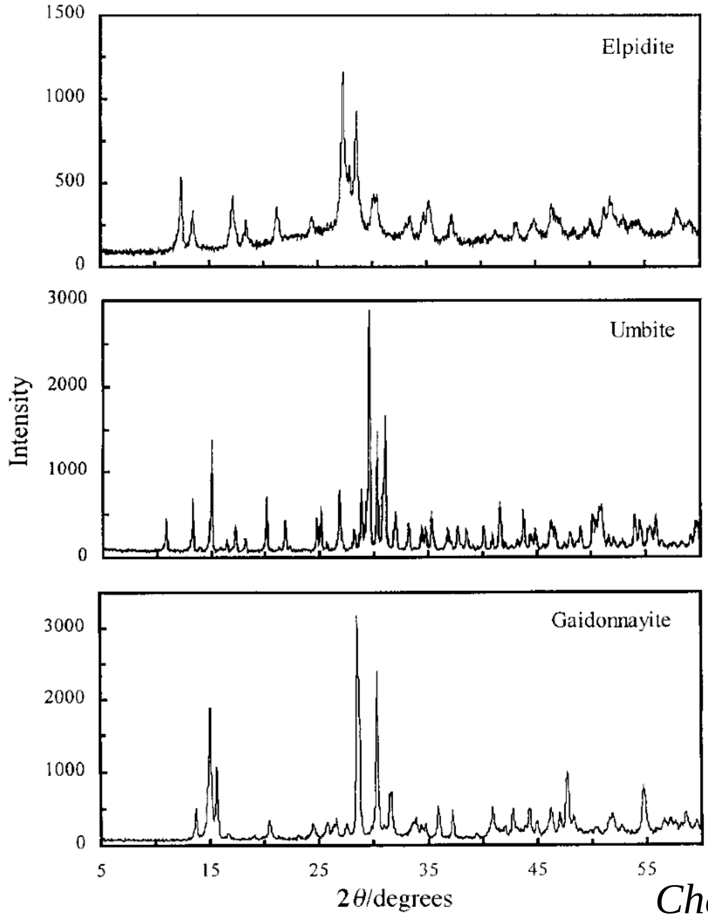


Ongoing and future work

1. Exploring new ion exchangers

Phases that can be thermally converted to **wadeite-type** phases will form potential ceramic wasteforms.

J. Am. Ceram. Soc., 84 [1] 153–60 (2001)



Elpidite
$Na_2ZrSi_3O_9\cdot3H_2O$

Umbite
$Na_2ZrSi_3O_9\cdot1H_2O$

Gaidonnayite
$Na_2ZrSi_3O_9\cdot2H_2O$

Further work:
- Sn-form
- Mixed (Ti, Zr, Nb, Sn)

Chem. Commun., 1999, 411–412

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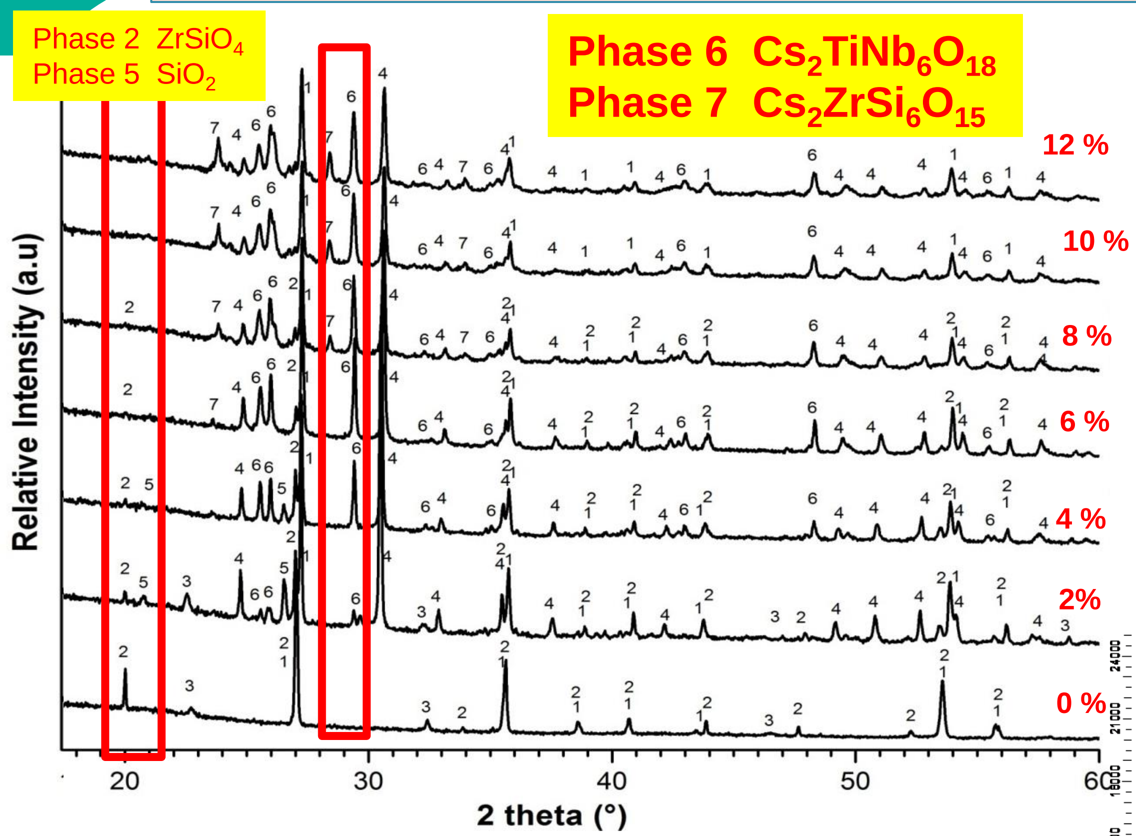
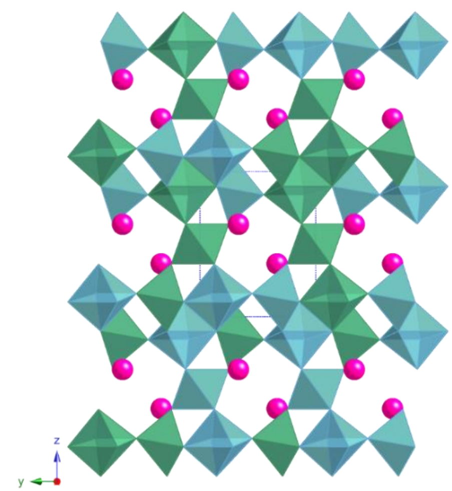
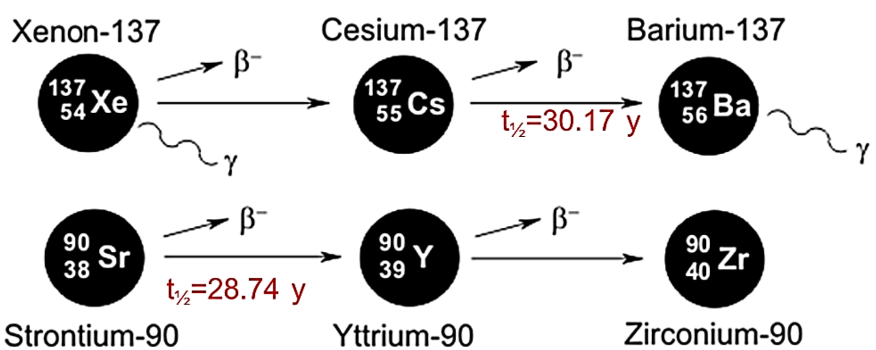
2. Modification-Nb substitution

Thermal conversion of Cs-loaded IONSIV by HIPing

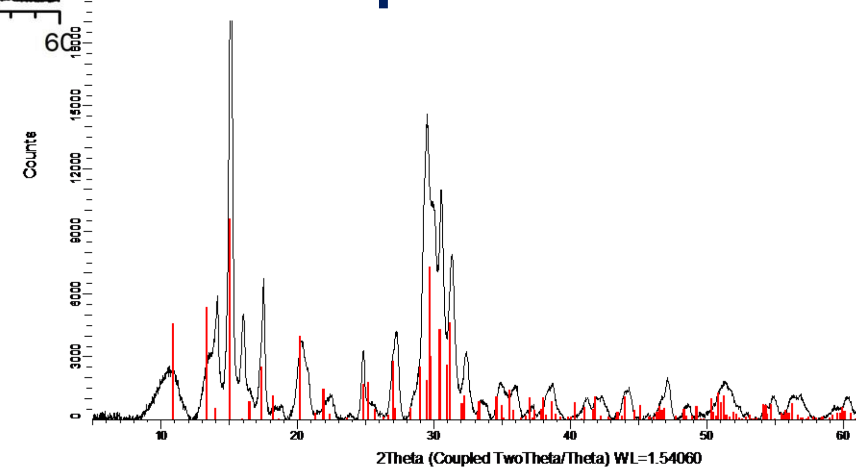


$Cs_2TiNb_6O_{18}$





Nb doped Sn-umbite



3. Atomistic modelling

- Simulation of Cs^+ exchange in CST using clayFF potentials (manuscript submitted)
- New potentials developed for Ti, Nb and Sn.
- Attempts to model different Sn systems to understand why umbite (AV-6) shows better ion exchange properties than kostylevite (AV-7).

Dr Paul Martin
Dr Mark Read

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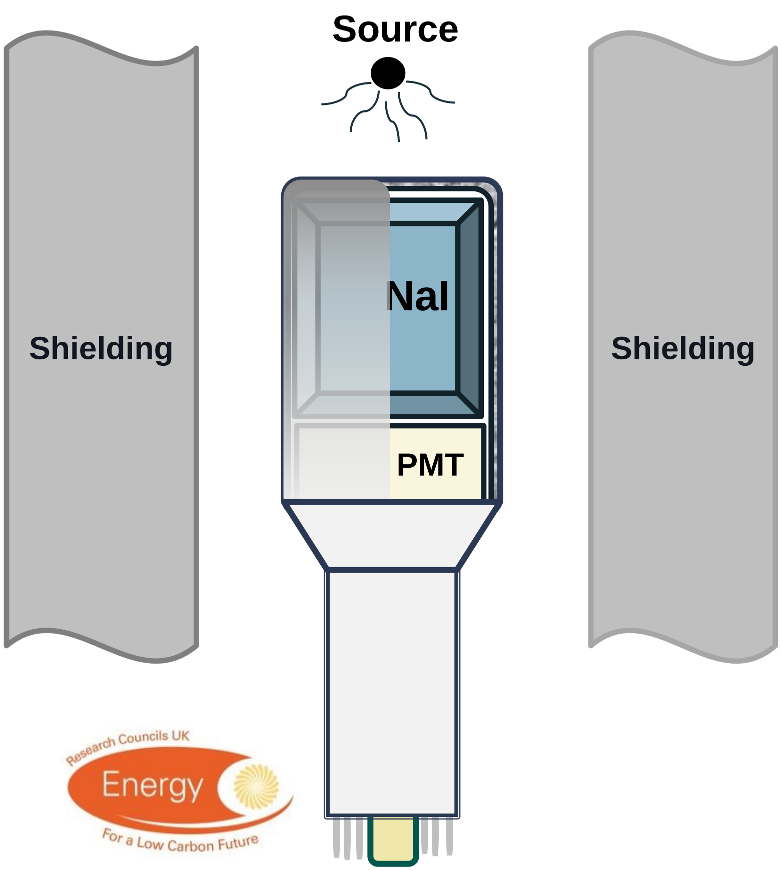
4. Realistic simulated conditions

Radioactive ^{85}Sr

gamma activity measurement

- *Ion exchanger*
- *Residual liquid*



- Low concentration of Cs and Sr
- Competing cations present

(numbers for ^{137}Cs and ^{90}Sr shown in Bq/ml, others in ppm) (PPM)

	Case 1	Case 2	Case 3	Case 4
pH	11.2	11	10	>10
^{137}Cs	9.06E-04	3.62E-01	3.02E-01	1.51E+00
^{90}Sr	1.51E-05	1.53E-03	5.67E-03	3.21E-02
Na	70	130	60	210
K	0.2	10	20	250
Ca	0.2	3	1.2	60
Mg	0.1	3	140	30
U		2	200	

Information provided by Dr S Kellet, Sellafield

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Acknowledgement

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