Synthesis of zirconogermanates with potential ion exchange applications

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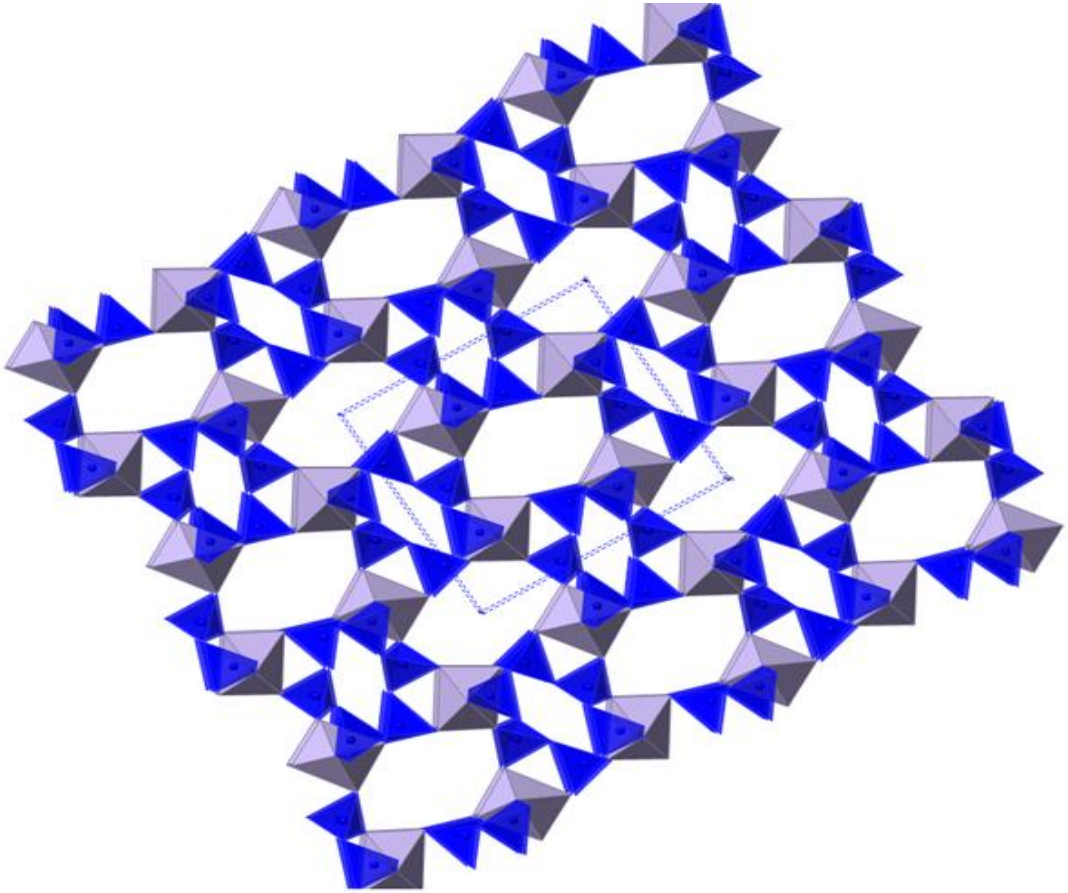
Introduction

- The need to design materials for effluent clean-up or environmental remediation is a key issue which needs to be addressed.
- These materials need to have high selectivity and exchange capacities , whilst being easy to process and dispose off.
- Zeolites have been the materials of choice however they are condition sensitive.
- This has led to the development of a different group of materials which have mixed octahedral-tetrahedral frameworks.

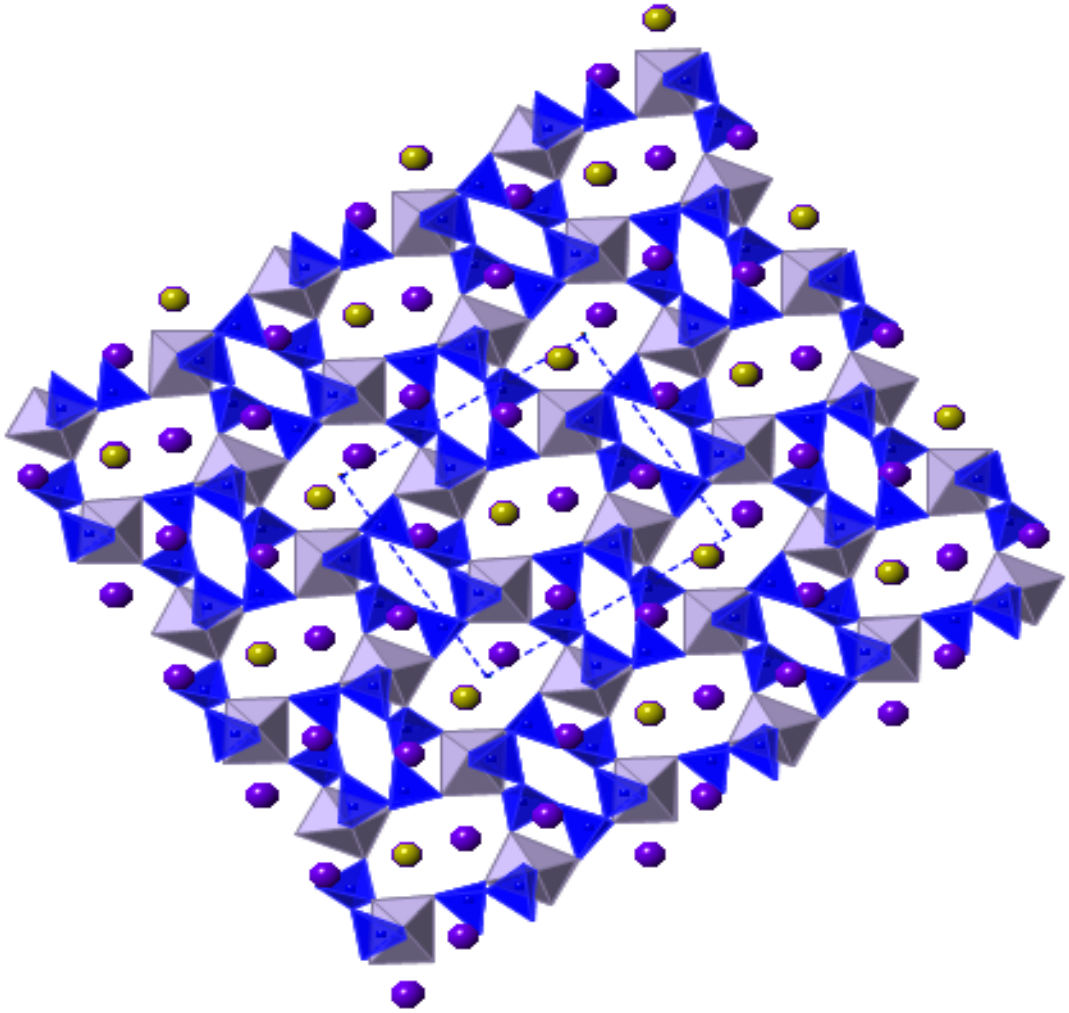
Octahedral-tetrahedral frameworks

- These materials contain both octahedral and tetrahedral oxide polyhedra.
- Some of these materials are naturally occurring.
- A wide range of materials have been synthesized with various different metal octahedra.
- These materials are microporous and have cations in the channels, commonly sodium and potassium. Hence the interest as potential ion exchange materials.

Name	Formula
AV-6	$K_2(Sn/Zr)Si_3O_9 \cdot H_2O$
AV-7	$Na_{0.5}K_{1.5}SnSi_3O_9.H_2O.$
AV-10	$Na_2SnSi_3O_9.2H_2O$
EMS-2	$Na_4K_4Sn_4Si_{20}O_{52}$ .12H_2O
AV-13	$Na_{2.26}$ $(Sn/Zr/Hf)Si_3O_9Cl_{0.26}$ .xH_2O



Structure of AV-7



Why germanium?

- Most of the previous work covered focuses on changing the octahedral metal ion.
- Variation of the tetrahedral component may allow for further tunability.
- Germanium is possible alternative to silicon as it is in the same group.

Project Aims

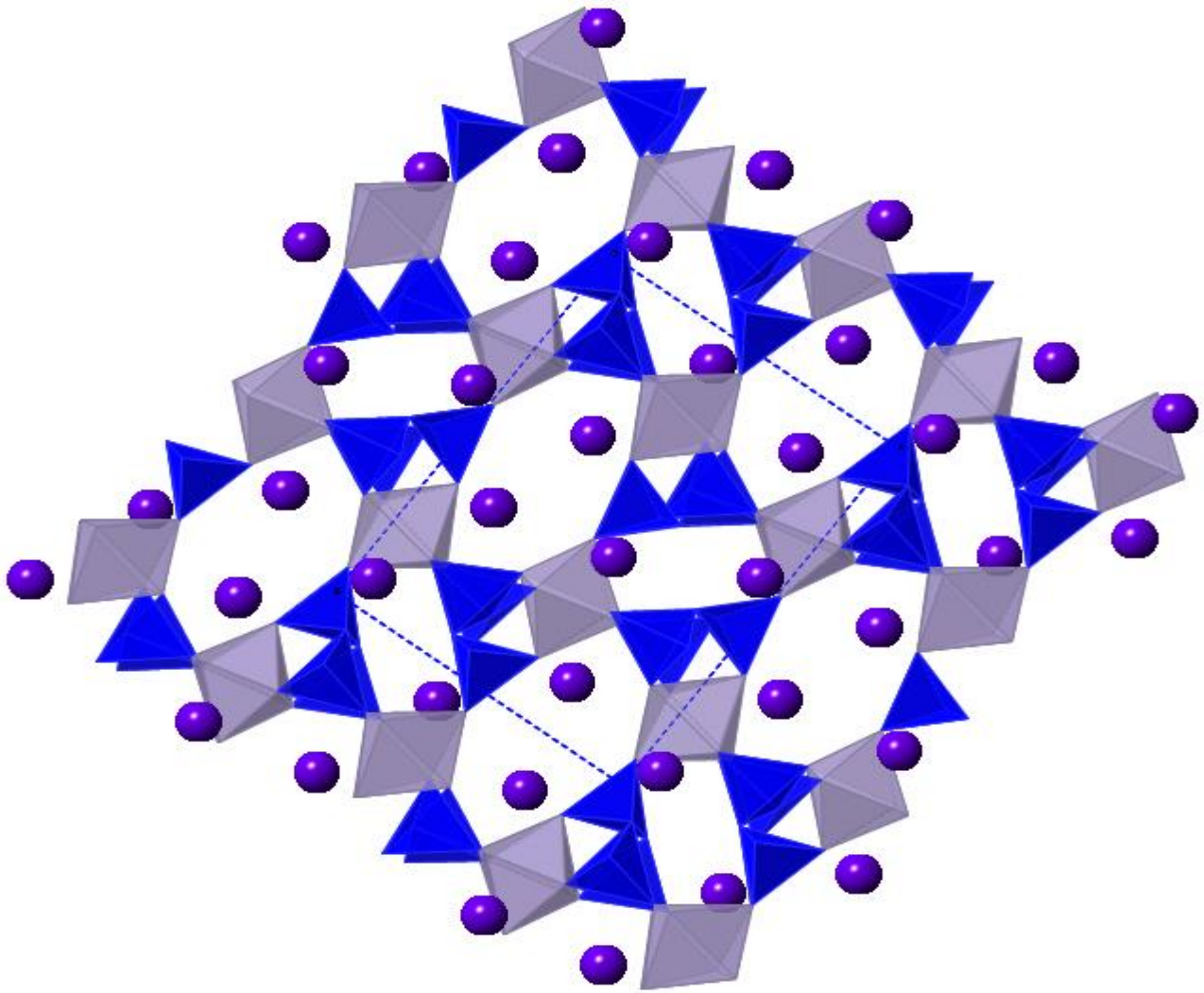
- To synthesise a range of different materials.
- Test these materials for any ion exchange properties.
- To analyse any decomposition products after high temperature treatment.

Zirconogermanates

- Current work focuses on 2 different zirconogermanates.
- The first material is the germanium derivative of the mineral Umbite, $K_2ZrSi_3O_9.H_2O$.
- The second is a layered zirconogermanate material.
- Both have been synthesized under hydrothermal conditions. (200^{0}C , 1-7 days)

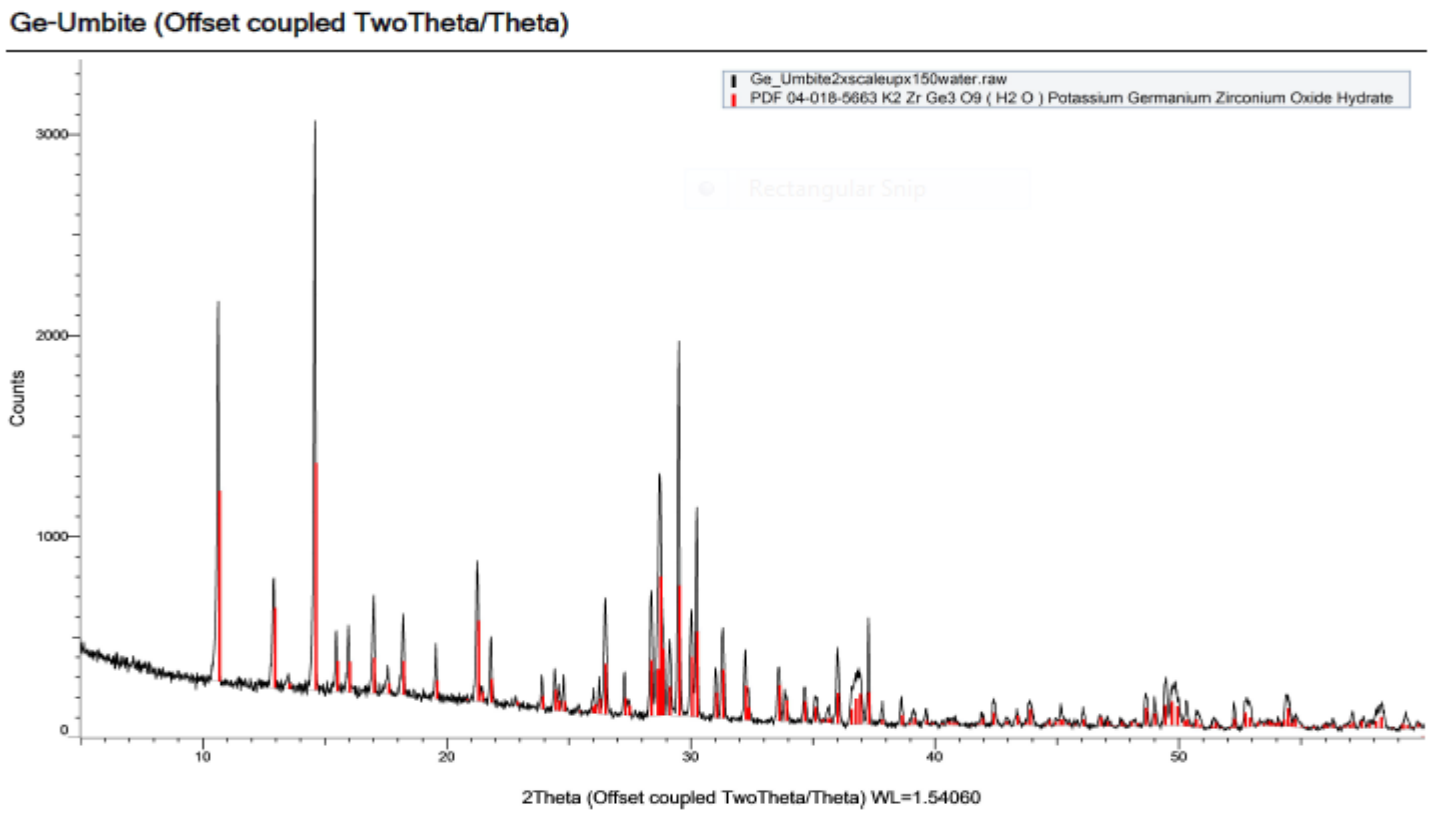
Ge-Umbite

- Umbite is a zirconosilicate mineral naturally found in Russia, $K_2ZrSi_3O_9 \cdot H_2O$.
- Initial attempts to synthesize the pure germanium form, by the direct replacement of silica for germanium dioxide resulted in wadeite, $K_2ZrSi_3O_9$.
- As a result a different approach was required to synthesize this material.



Structure of Umbite

- Using a batch composition found in the literature[1], which used a much more diluted gel resulted in Ge-Umbite.



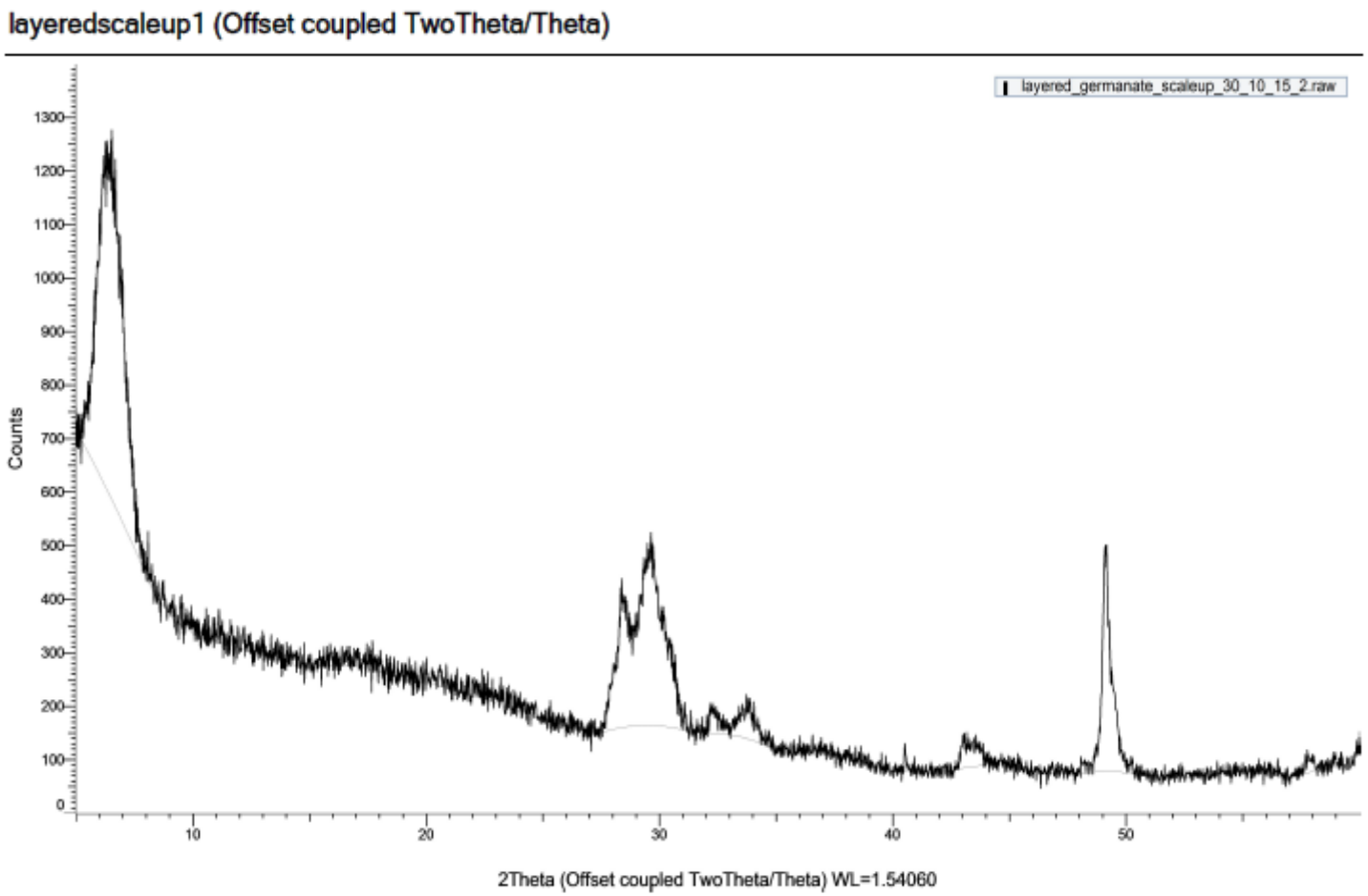
1.Plevert et al , Inorg.Chem,2003,**42**,5954-5959

However…

- The level of dilution of the starting gel results in a very small yield of a pure product.
- The result of this is that no ion exchange tests can be performed until the synthesis can be scaled up.

Layered zirconogermanates

- Another interesting material is a layered zirconogermanate.
- This material has been more extensively studied than Ge-Umbite however it has not had its structure solved.
- The original paper reports a sodium form ($Na_2Zr_5Ge_2O_{15}.8H_2O$) and the proton form from acid treatment ($H_2Zr_5Ge_2O_{15}.6H_2O$).
- The proton form has had its ion exchange properties explored in the literature.


layeredscaleup1 (Offset coupled TwoTheta/Theta)
layered_germanate_scaleup_30_10_15_2.raw
Counts
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
10
20
30
40
50
2Theta (Offset coupled TwoTheta/Theta) WL=1.54060

Early XRF data

Element	Wt%	Ratio
Zr	66.22%	3.5
Cs	18.73%	0.7
Ge	14.91%	1
K	5.01%	0.6

Element	Wt%	Ratio
Zr	58.71%	3.5
Ge	13.50%	1
Sr	12.21%	0.8
K	3.47%	0.5

Conditions- 0.1M nitrate solution, 24 hour shaking.

Future work

- Work will focus on the scaling up of the Umbite synthesis. Following this ion exchange studies will be undertaken.
- Partial germanium doping of Umbite and refinement of the data.
- Further ion exchange tests on the layered material.
- Analysis of thermal decomposition products of both materials.

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