

Synthesis and Analysis of Ion Exchange Materials

By Michael Sarahan

What kinds of Ion Exchange Materials?

- Ion exchange materials studied this summer were pyrochlores and Nasicon
- Vanadium silicate/germanate clusters linked via amines were also synthesized

First Up: Pyrochlores

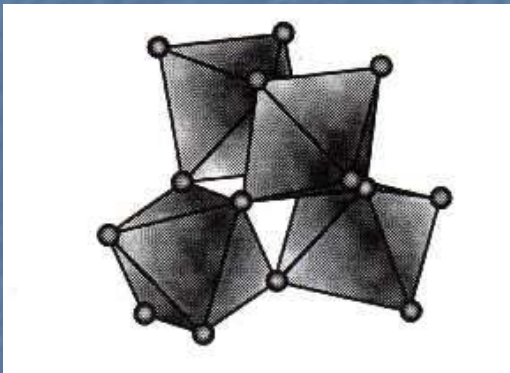
- WEEEE!



What are Pyrochlores?

- Pyrochlores get their name from the mineral that they have a identical structure to
- General composition:
 $A_2B_2O_6O'$
 - A=rare earth element, or element with inert lone pair
 - B=transition metal or post-transition metal
- Defect pyrochlores, in which A or O' sites are vacant, can be ion exchangers
- Hydrothermal synthesis yields more defects than high temperature synthesis

Pyrochlore structure

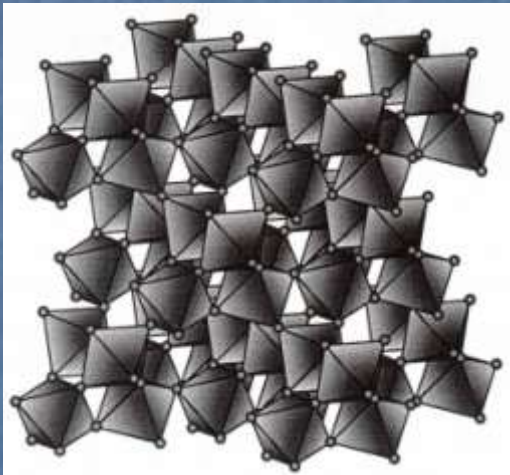


- Cubic Crystal structure

- Fd-3m* space group

- $a \sim 10.3 \text{ \AA}$

- $Z = 8$



- Four corner sharing BO6 octahedra connected at vertex in center

- A2O' chain penetrates into octahedral hole of the structure

- A cations are eight-coordinated to the six BO6 oxygens and two O' atoms

Why Pyrochlores?

- The purpose of experimentation with pyrochlores was to test the ion exchange affinity toward Ni^{2+} , Co^{2+} , Mn^{2+}
- Previous research indicates that pyrochlores are potentially useful in nuclear waste remediation because of their ion exchange properties*

*T. Moller, A. Clearfield, R. Harjula.

Selecting samples for Ion Exchange

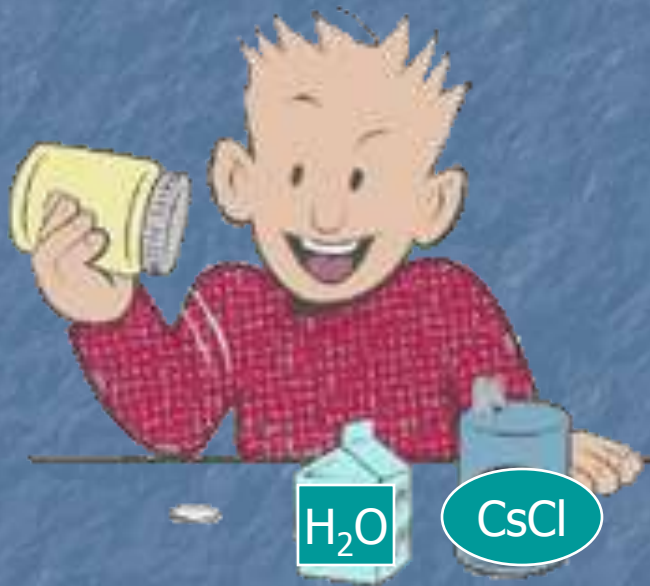
Criteria

- Single phase
- Chemical composition
- High crystallinity for structure refinement

Sample compositions

<u>Sample</u>	<u>Elements</u>	<u>Ratio</u>
MG01-01-2	Na:Sb:W	0.3 : 1.0 : 0.6
MG01-04-2	Na:Ti:W	1.6 : 1.0 : 3.3
MG01-23-1	Na:Ti:W	0.6 : 1.0 : 1.6
MG01-23-4	Na:Ti:W	0.7 : 1.0 : 1.6
MG01-24-3	Na:Sb:W	1.2 : 1.0 : 1.7
MG01-26-2	Na:Sb:W	1.1 : 1.0 : 1.9

The Process of Ion Exchange



- Pyrochlore samples were shaken for ~48 hours with solutions containing cations such as Cs, Sr, Mn, Ni, or Co
- The solutions were filtered, and both the solid & liquid was collected

Methods for Analysis

- AA Spectroscopy of solutions before and after ion exchange
- X-ray diffraction analysis of starting materials and ion-exchanged materials
- Microprobe analysis of ion-exchanged materials



Uptake values for MG01-26-02

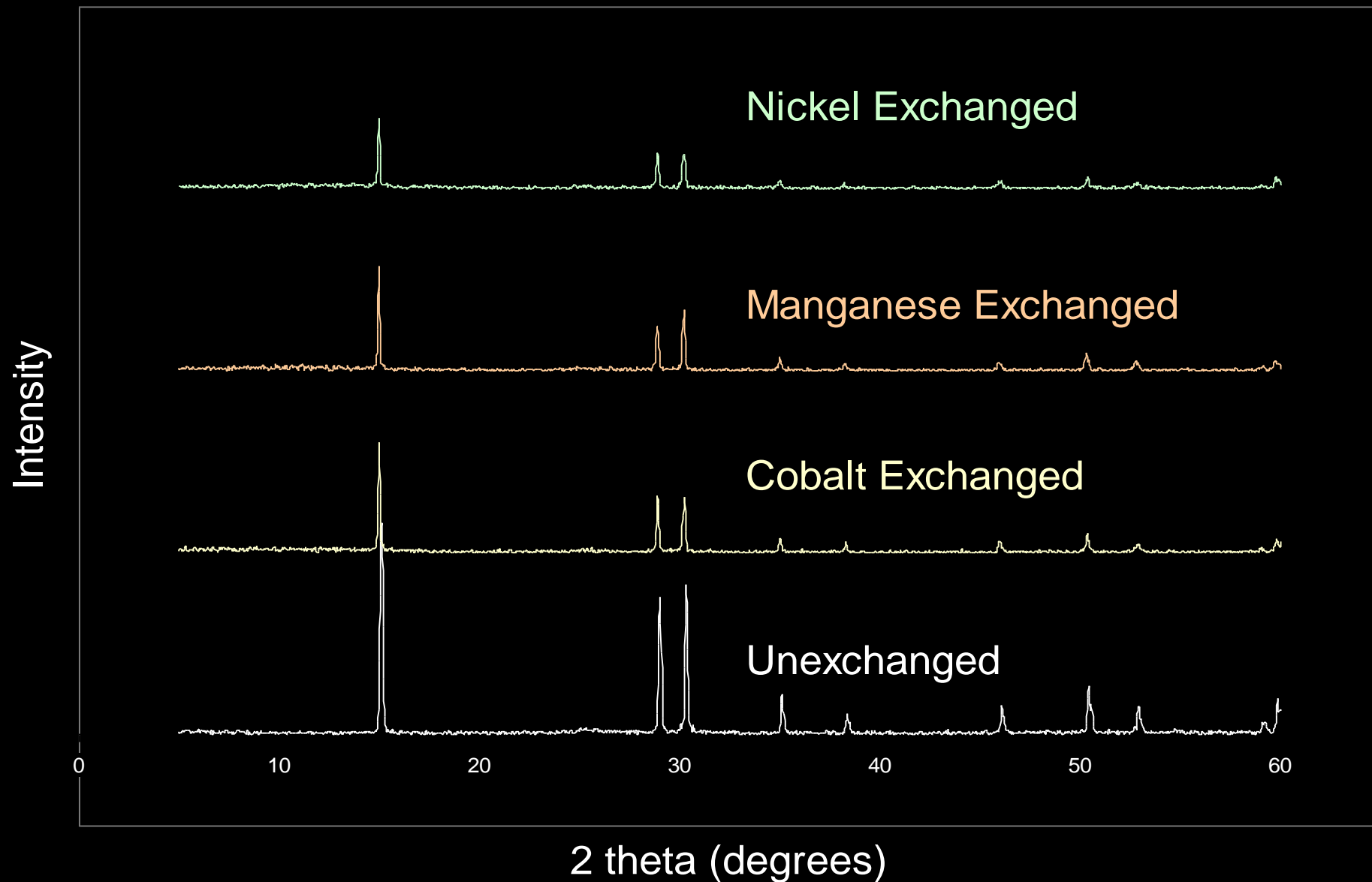
<u>Ion exchanged:</u>	Uptake (mmol/g)
Ni ²⁺ , from Ni(NO ₃) ₂	.0142
Cs ⁺ , from CsCl	0
Sr ²⁺ , from SrCl ₂	.500

And Now...

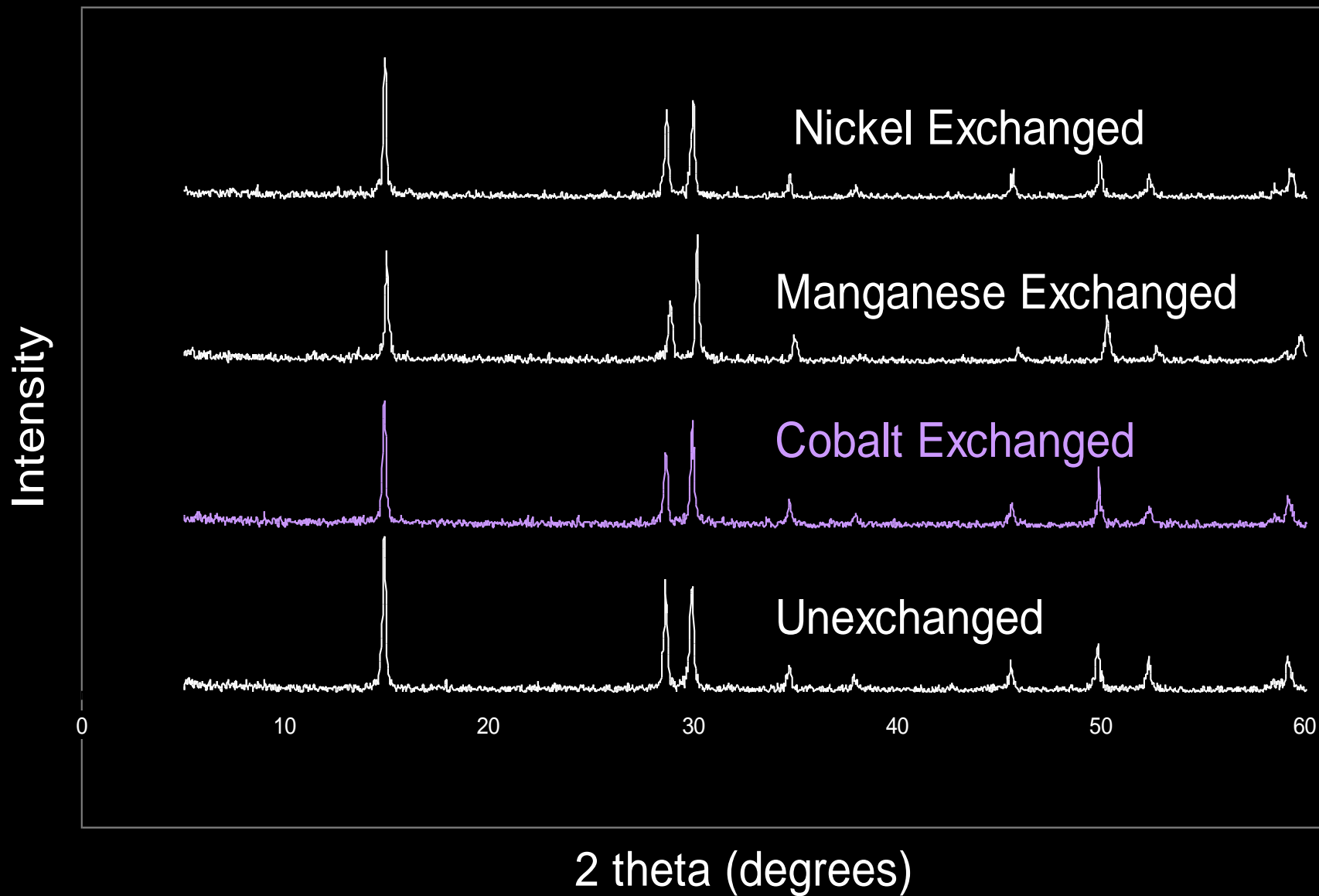


- Some GRAPHS!

XRD patterns of MG01-23-01



XRD patterns of MG01-26-01



Next: Nasicon

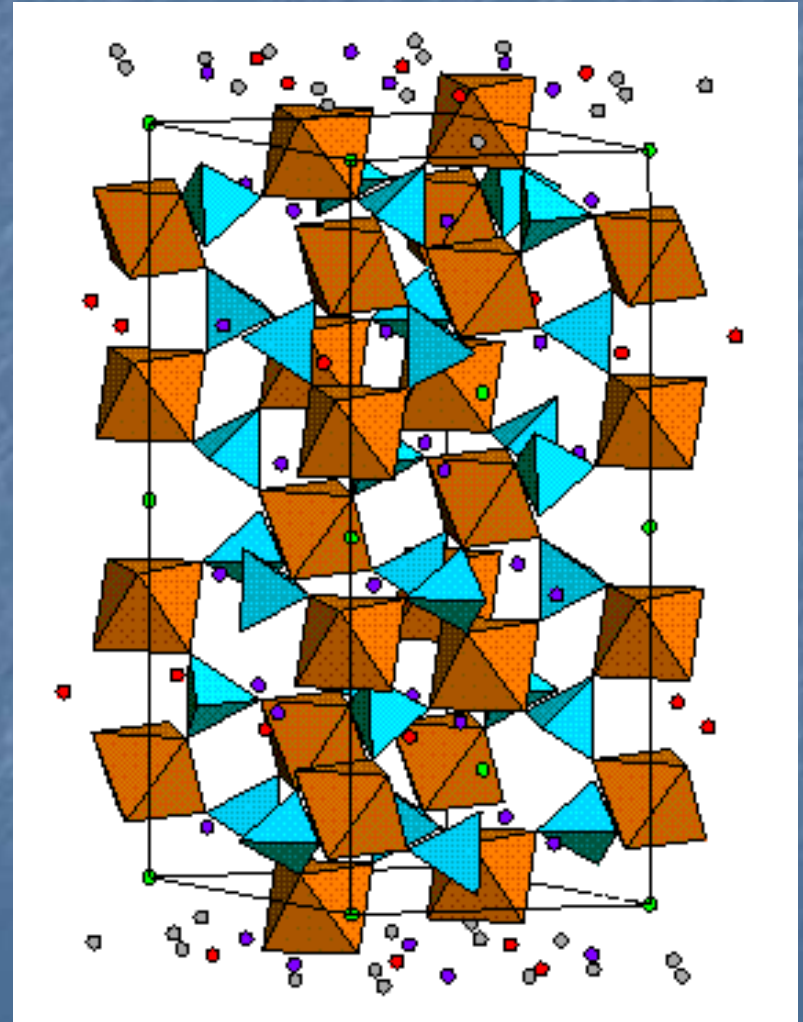
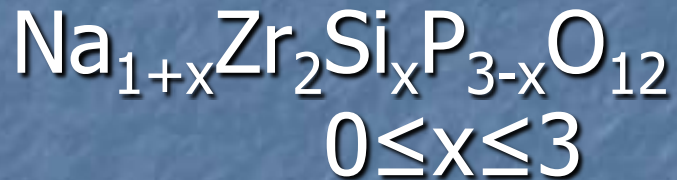
- WEEEE!!!



Nasicon

- NaSICON stands for **Na Super Ionic Conductor**

- Gen. Formula:



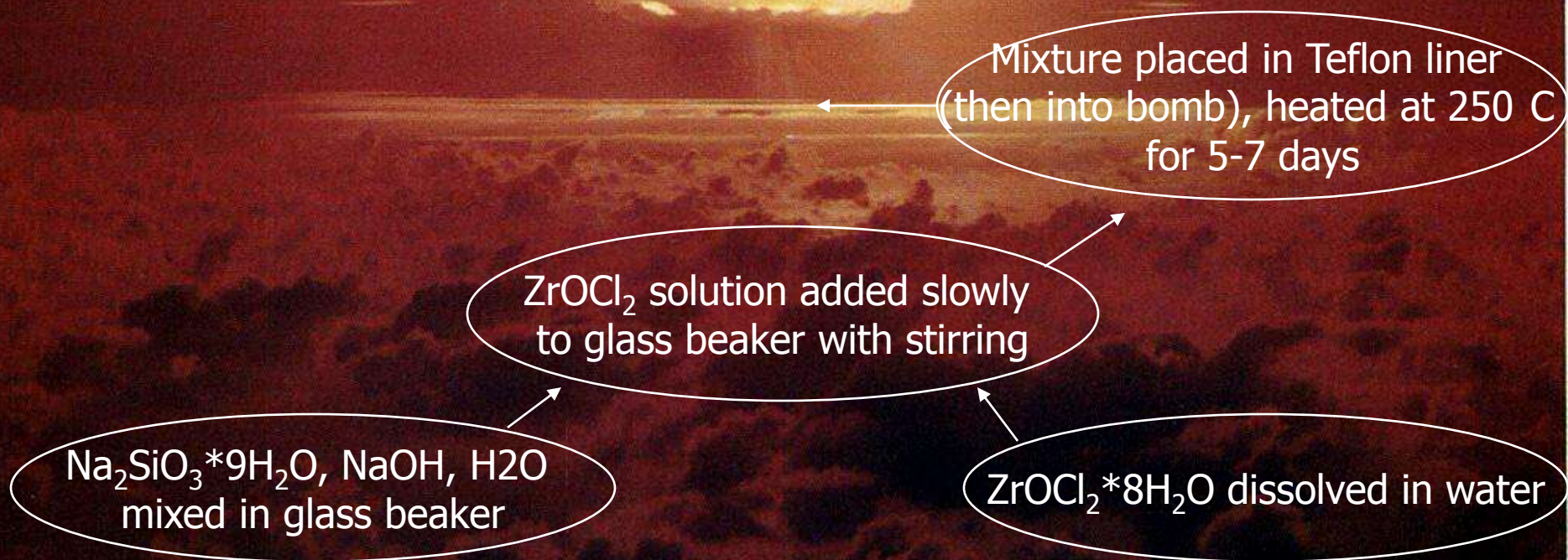
Applications of Nasion

- Gas sensors
- Sodium ion absorption
 - Protection of sodium-sensitive catalysts
 - Removal of sodium from waste streams

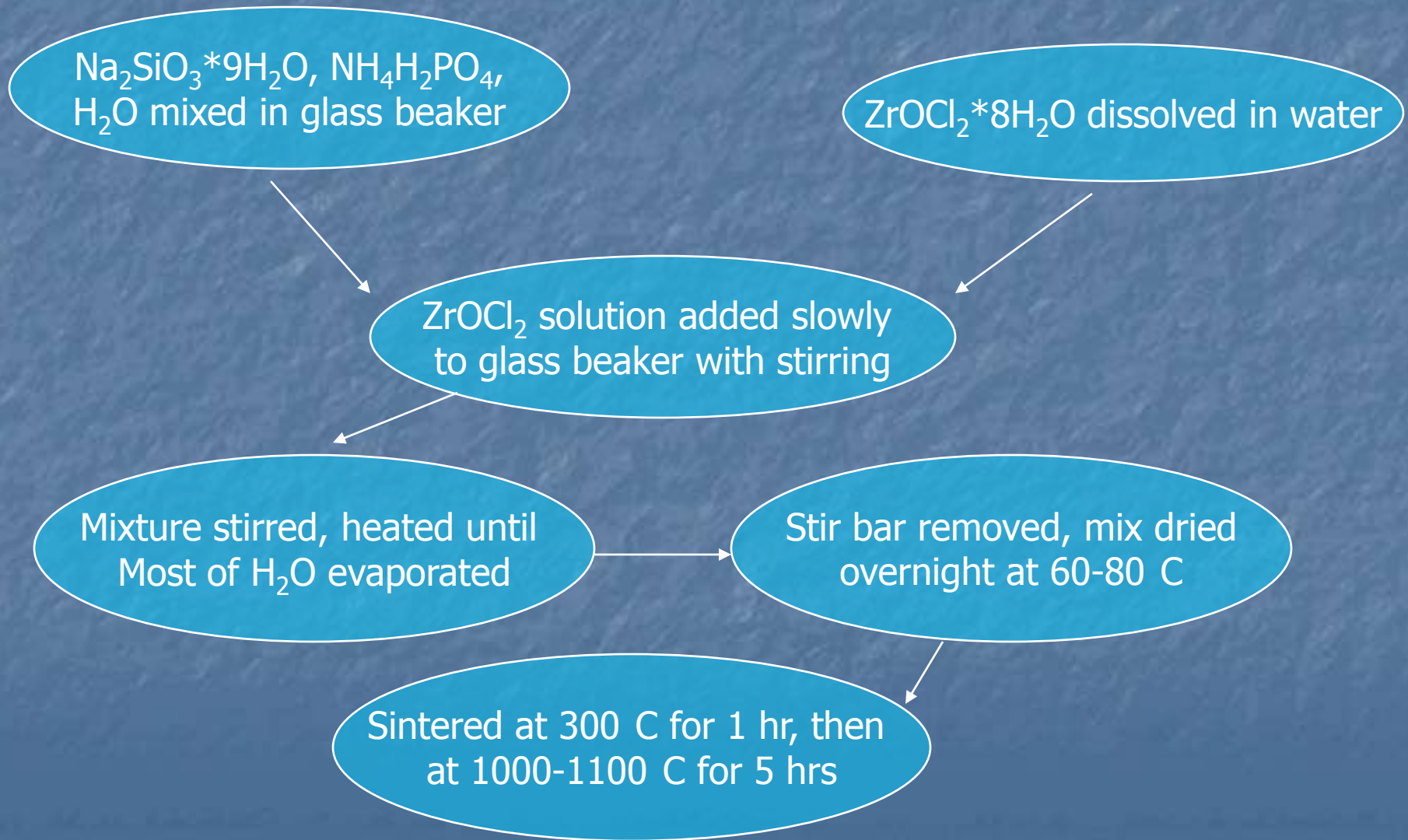
Synthesis of Nasion

- Synthesized both hydrothermally and by high temperature sintering
- Pure product is difficult to obtain
 - ZrO_2 always a product

Hydrothermal Synthesis



High Temperature Synthesis

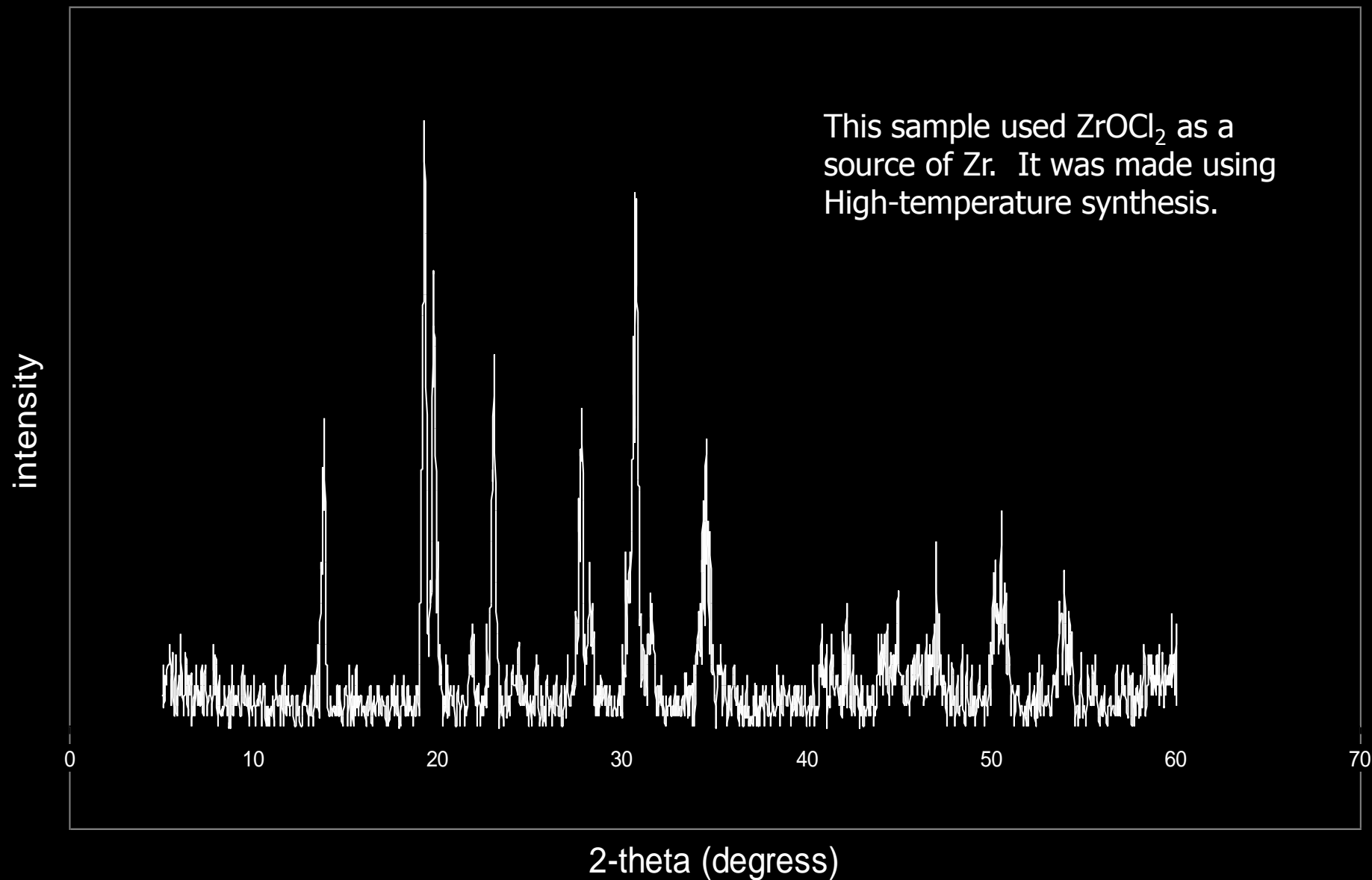


And Now...

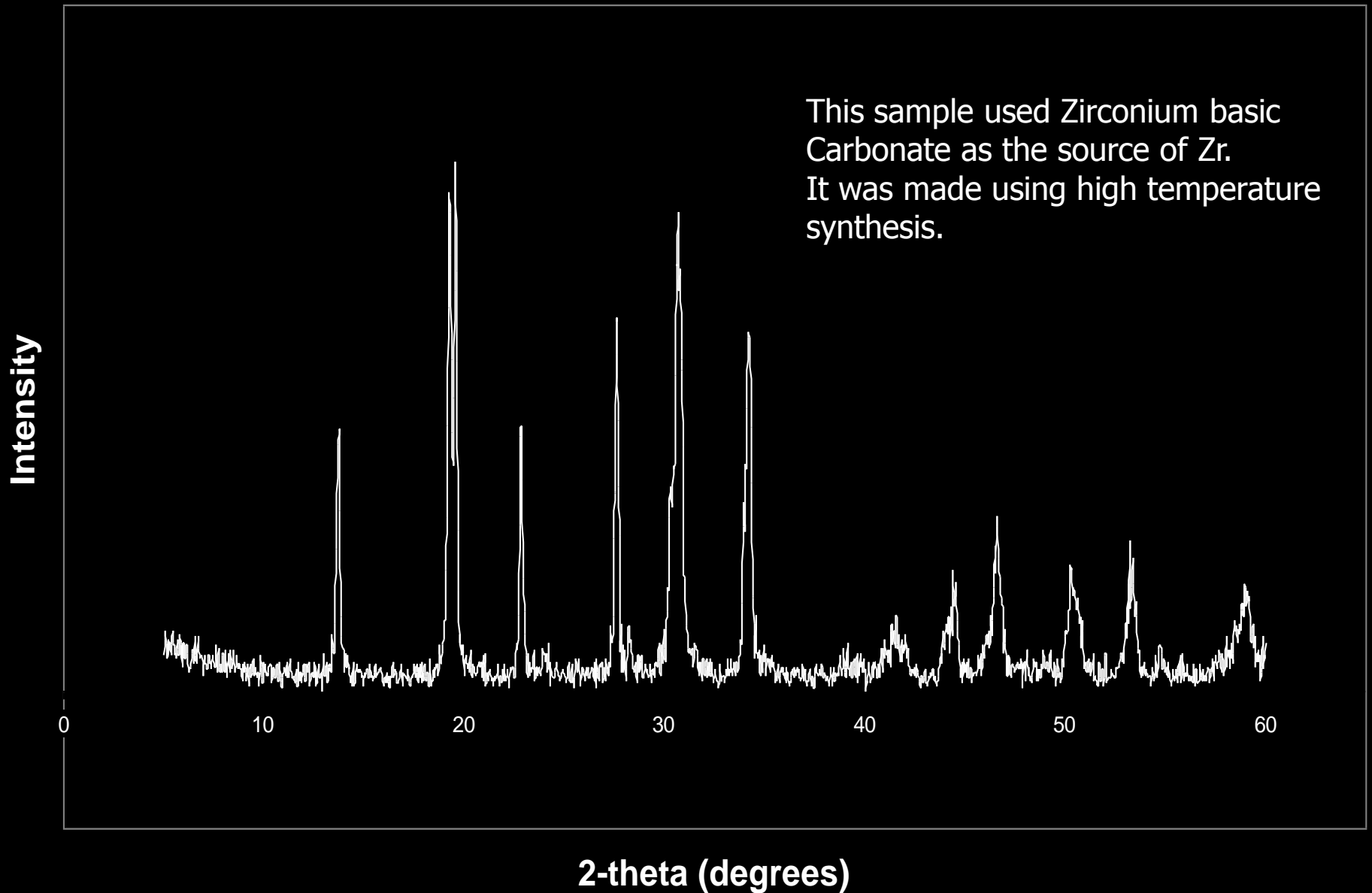


- More GRAPHS!

MCS01-34 XRD Powder Pattern



MCS01-45 XRD Powder Pattern



Next: Vanadium Germanate/Silicate Clusters Linked With Amines

- WEEEE!!!



Vanadium silicate/germanate clusters linked with amines

- General idea is to link vanadium germanate/silicate clusters with diamino or multiamino organic molecules, forming frameworks with tunnels

Hydrothermal Synthesis

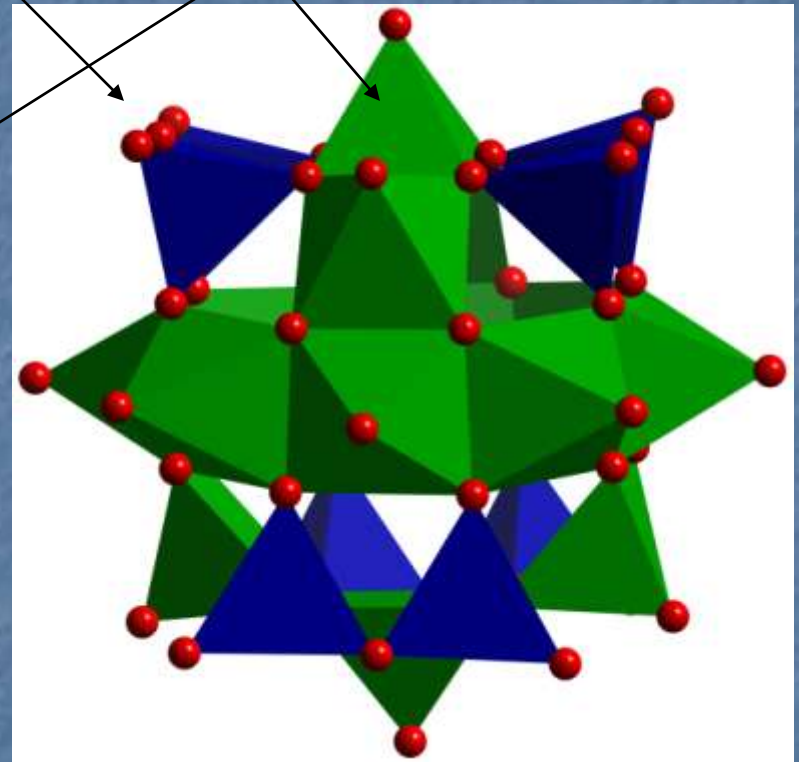
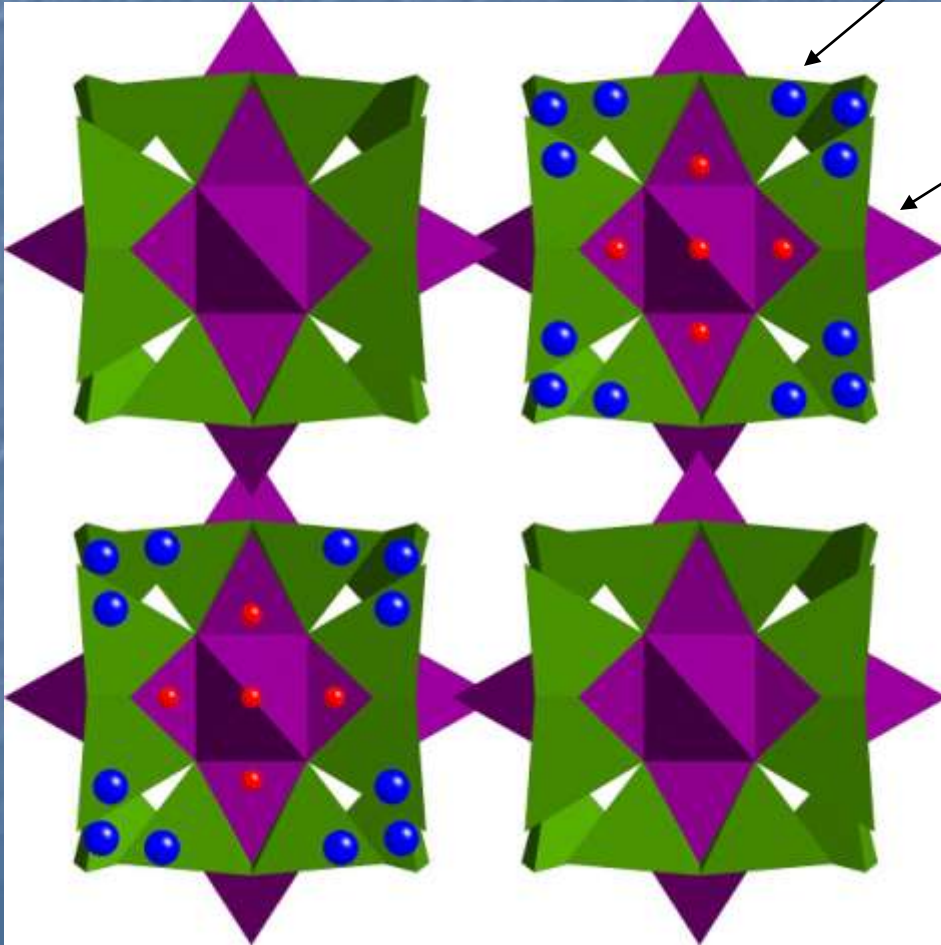


- Reagents mixed in water, generally overnight.
- Mix placed in Teflon liner, then into Parr autoclave
- Left in oven @ 170-180°C for 5-7 days
- Crystals are desirable
 - Easier structure solution

Vanadium Germanate Clusters

GeO₄ tetrahedra

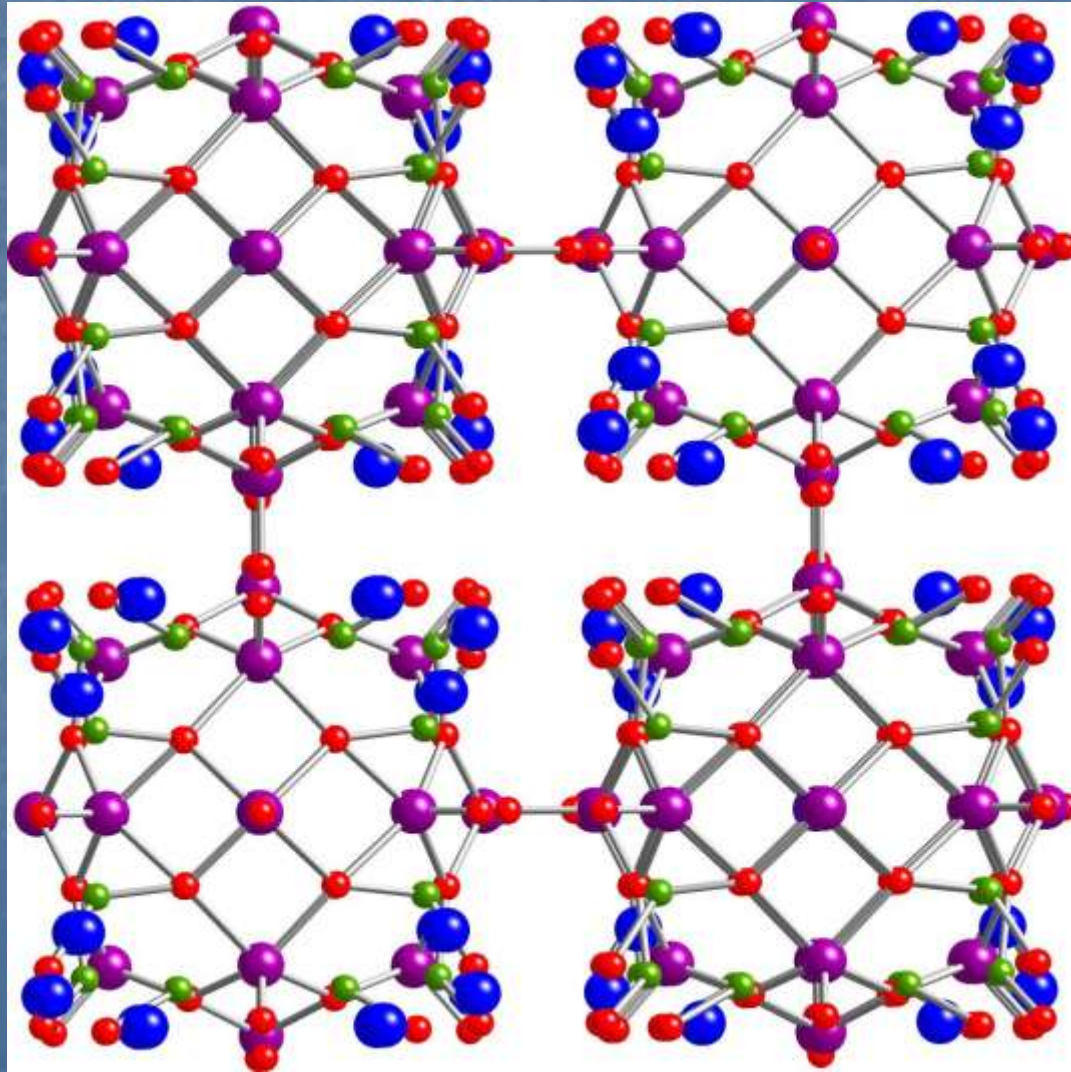
VO₅ pyramids



Cluster Details

- Space Group: Fm-3
- $a=19.818(7) \text{ \AA}$
- Volume: 7784.4 \AA^3
- twinned, disordered

Vanadium Silicate Cluster



Cluster Details

- Space Group: FM-3
- $a=19.566(7) \text{ \AA}$
- Volume: 7491.2 \AA^3
- twinned, disordered

Potential of Materials

- These materials show promise as ion exchange materials because of their tunnels.

References

- Teresia Moller, Abraham Clearfield, and Risto Harjula. *Preparation of and Ion Exchange of Cesium and Strontium on Hydrous Mixed Metal Oxides of Sb, Nb, Si, Ti and W with a Pyrochlore Structure*. Microporous and Mesoporous Materials, 2002.

