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SAND2009-5648C

The Advanced Fuel Cycle Initiative

Thermochemistry of New Fission Product Waste Forms

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Project Objectives

- Establish ceramic waste forms for disposing of Cs, Sr and minor actinides
  - consisting of transition metal oxides loaded *in-situ*
  - minimize additional processing steps
  - minimize waste volume
  - durable waste forms for all cations and their decay products
- Determine structure of ceramic waste form candidates using
  - solid state nuclear magnetic resonance (NMR),
  - scanning electron microscopy with energy dispersive chemical analysis (SEM/EDS)
  - single crystal and powder X-ray diffraction (XRD)
  - powder neutron diffraction
- Use high temperature oxide melt solutions of key compounds to determine:
  - enthalpies of formation
  - entropies of formation
  - free energies of formation
- Develop structure-property relations to provide predictive capabilities regarding key performance parameters.

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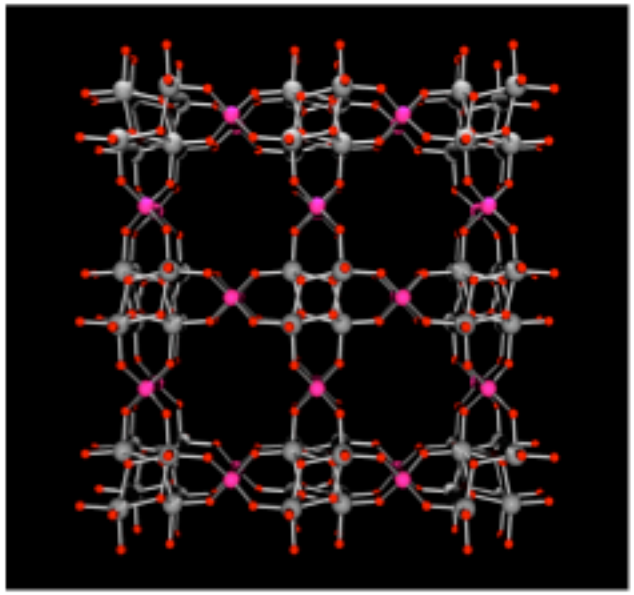
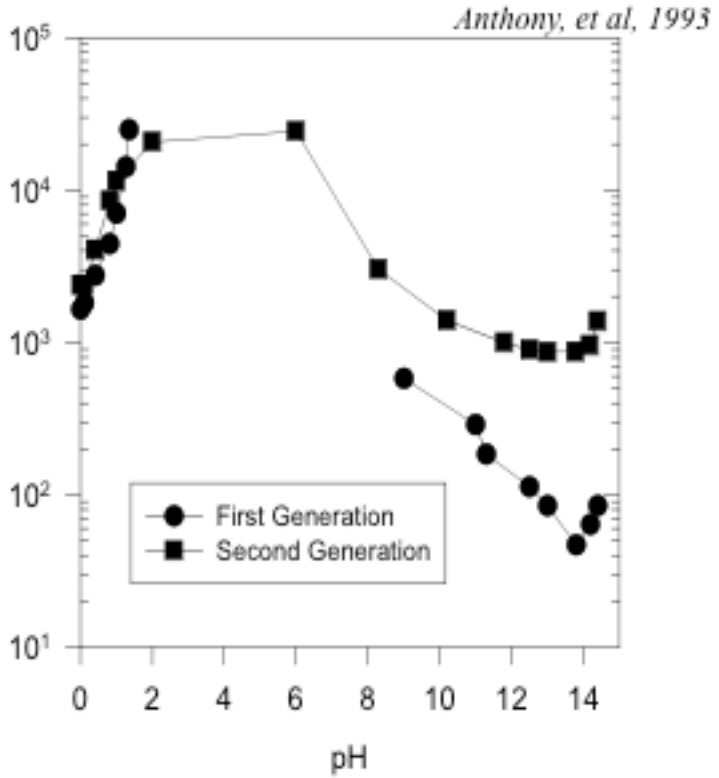
Background: SNL CSTs for ^{137}Cs Capture and Heat treatment to form durable waste forms

CST ion exchanger

Nenoff, 1996



Distribution Coefficient of Cs on CST

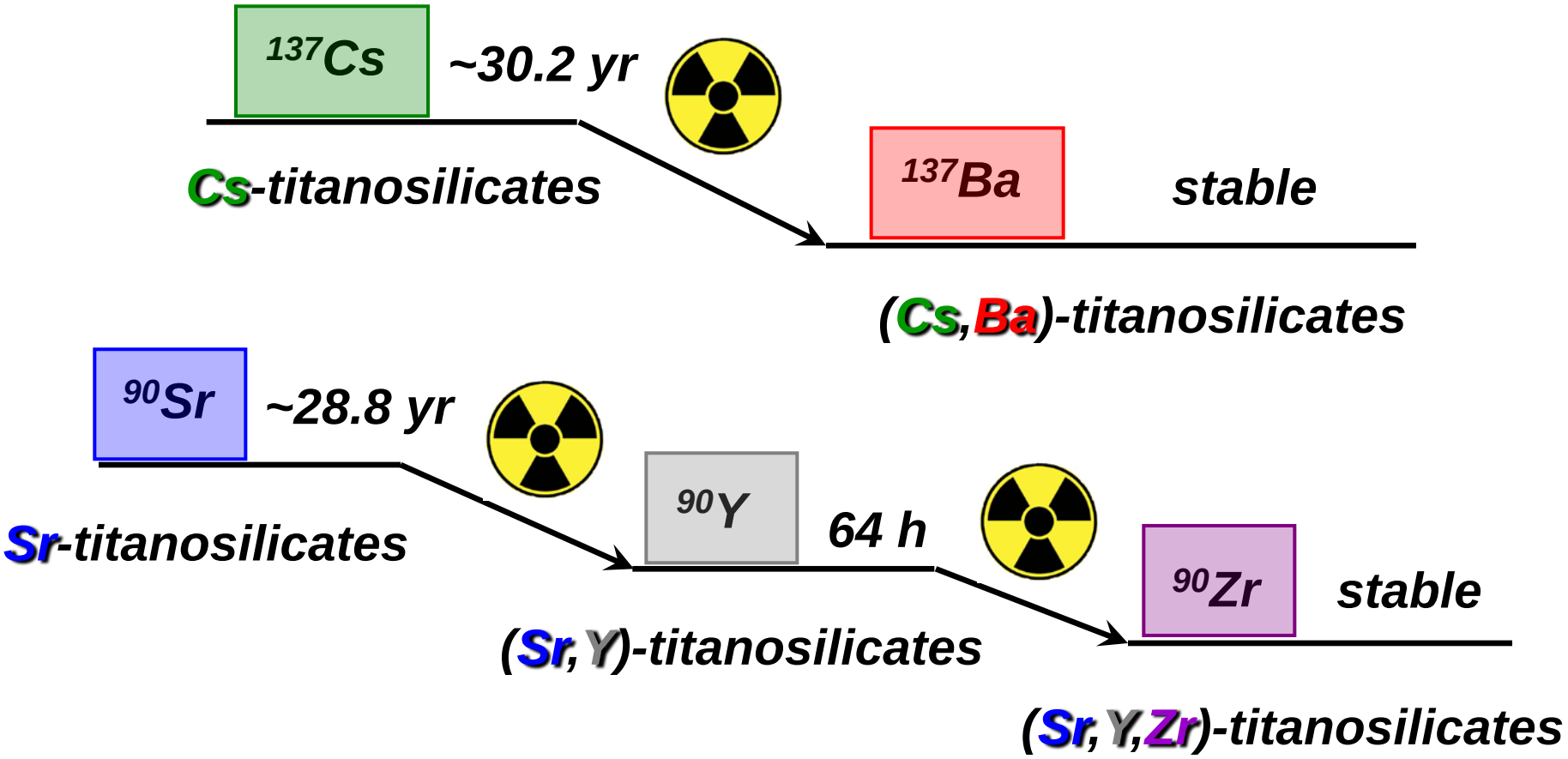


CST properties:

- Removes 1 part Cs per 100,000 parts Na
- Stable over entire pH range
- Stable in extreme environments

1996 R & D 100 award
1996 Team ERA

Decay Products



Although the concentration of Y at secular equilibrium is very small

$Sr^{2+} \rightarrow Y^{3+} \rightarrow Zr^{4+}$

How does the structure and its stability respond to these changes?

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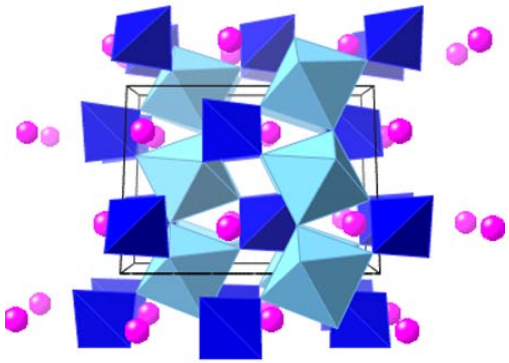
Waste Form Case Studies

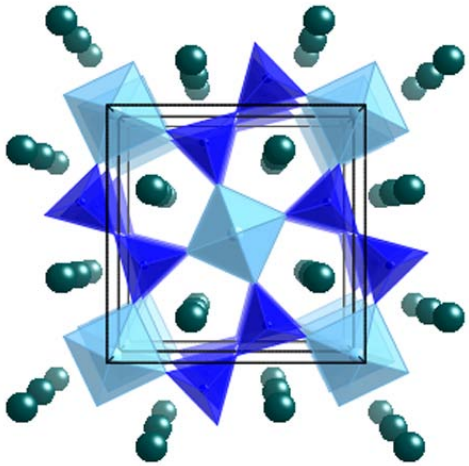
Neosilicates
Orthosilicates
Isolated $[SiO_4]^{4-}$

Titanite (sphene)
$CaTiSiO_5$
$SrTiSiO_5$
$BaTiSiO_5$



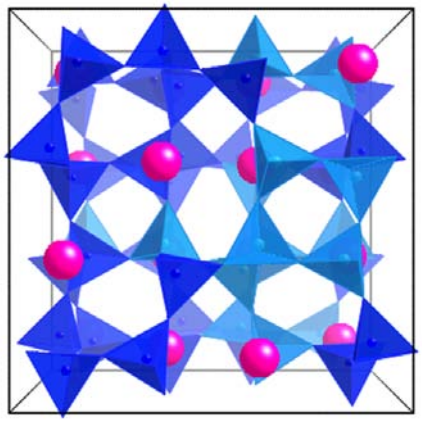
Sorosilicates
Isolated double tetrahedra $[Si_2O_7]^{6-}$

Melilite group
Fresnoite
$Ba_2TiSi_2O_8$
$Sr_2TiSi_2O_8$



Tectosilicates
3-D framework
SiO_2 tetrahedra

Feldspathoid group
Pollucite
$CsTiSi_2O_{6.5}$
$(CsAlSi_2O_6)$



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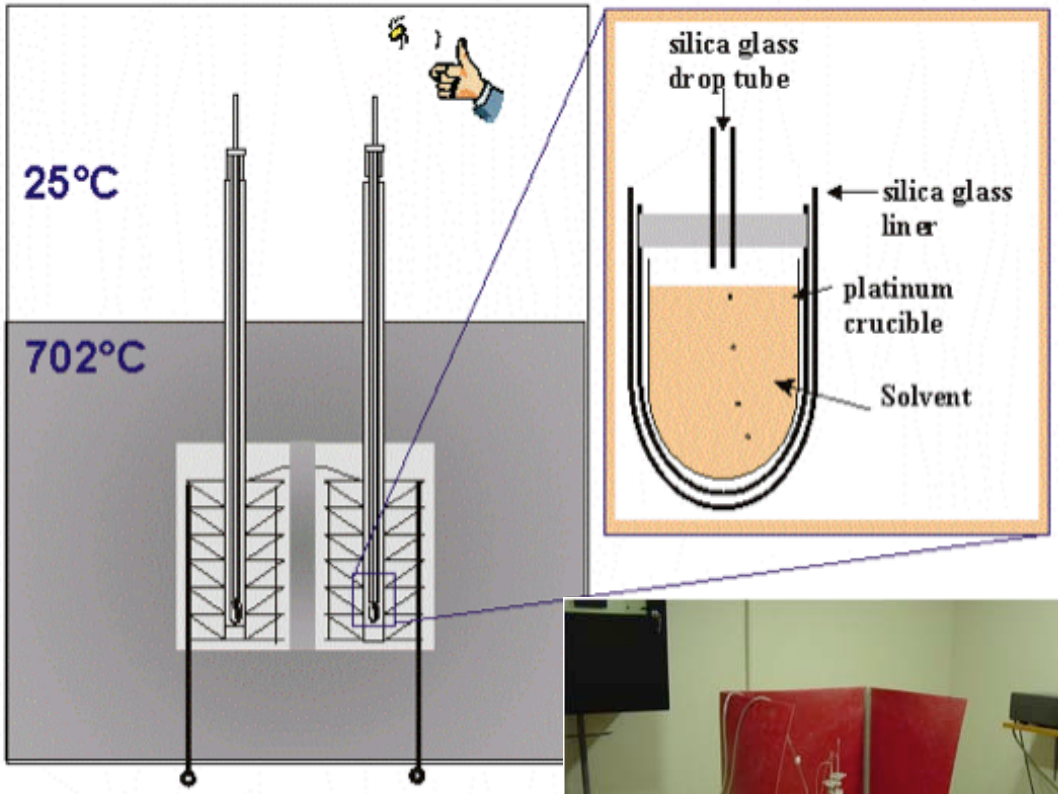
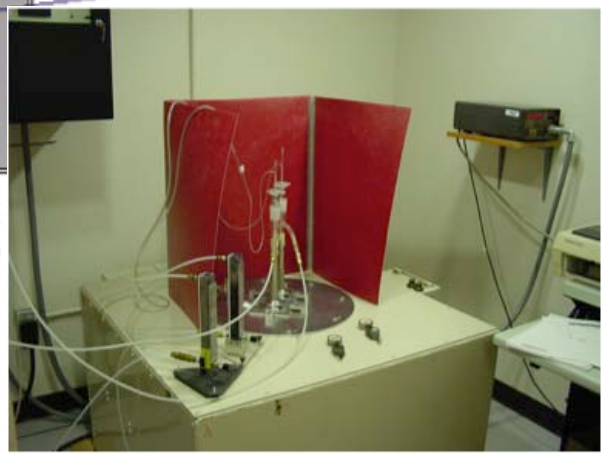
High Temperature Oxide Melt Solution Calorimetry

- Dissolve oxide samples 5-15mg in a molten oxide solvent 20g form a dilute solution
- Difference in heat of solution of reactants and products gives heat of reaction
- Oxidative reactions for nitrides sulfides, selenides, carbides
- Unique to Peter A. Rock Thermochemistry Laboratory at UC Davis



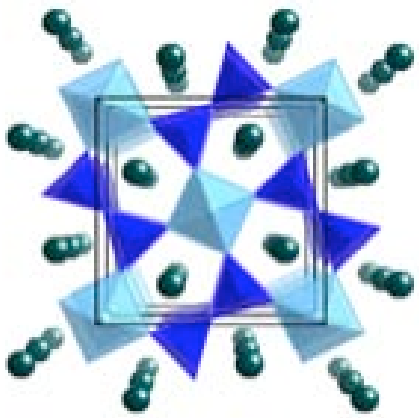


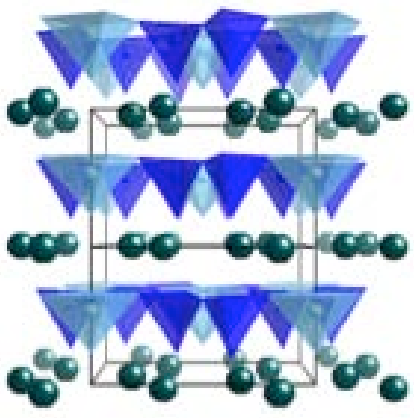
UCDAVIS Thermochemistry Facility

Fresnoite

- Barium titanosilicates are possible oxide forms for immobilization of short lived fission products in radioactive waste.

- $Ba_2TiSi_2O_8$ (fresnoite) and $BaTiSiO_5$ (Ba-titanite) samples were prepared by a solid state synthesis.





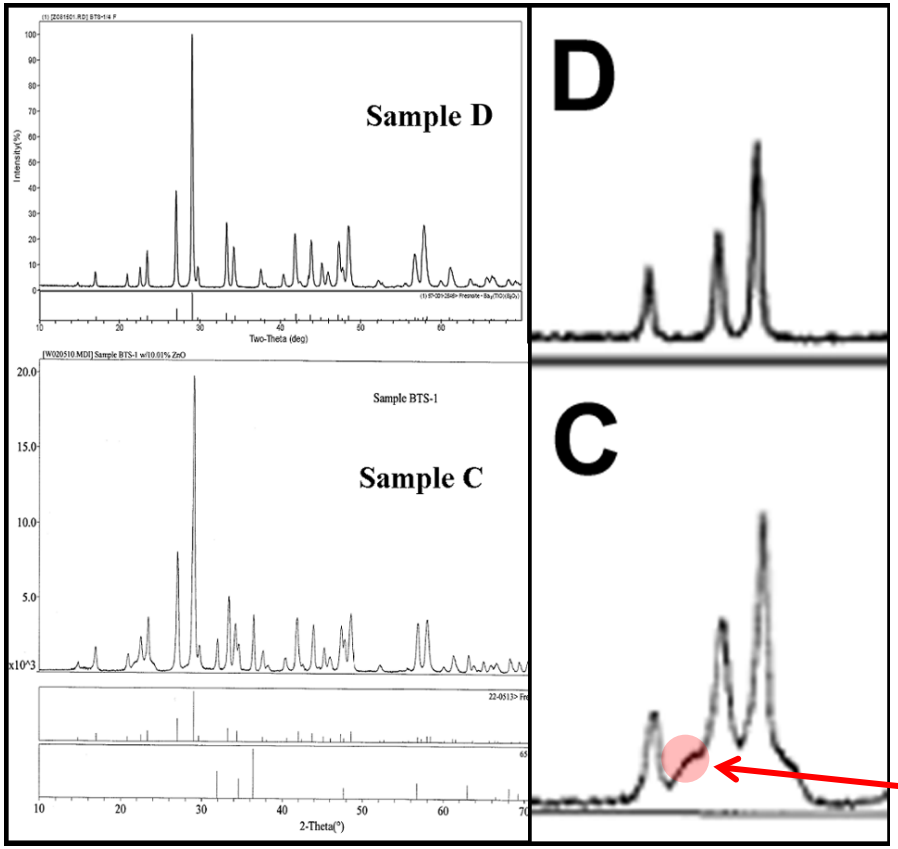
Moore, P. B.; Louisnathan, J. Science, **156**, 1361 (1967).

Melilite Structure: $A_2B(T_2O_7)$
unique Ti(IV) ion with 5-fold coordination (Nature, 1996, 381, 401)

Contains Isolated double tetrahedra $[Si_2O_7]^{6-}$

Fresnoite: $Ba_2(TiO)[Si_2O_7]$

Fresnoite ($Ba_2TiSi_2O_8$)



Fresnoite samples (provided by Schott):

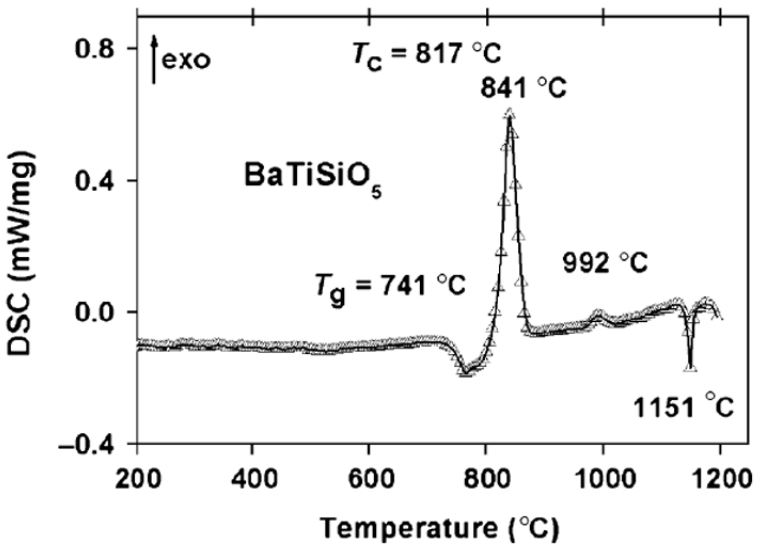
A (100% glass)
B (91%)
C (13%)
D (7%)
E (0%; complete crystal)

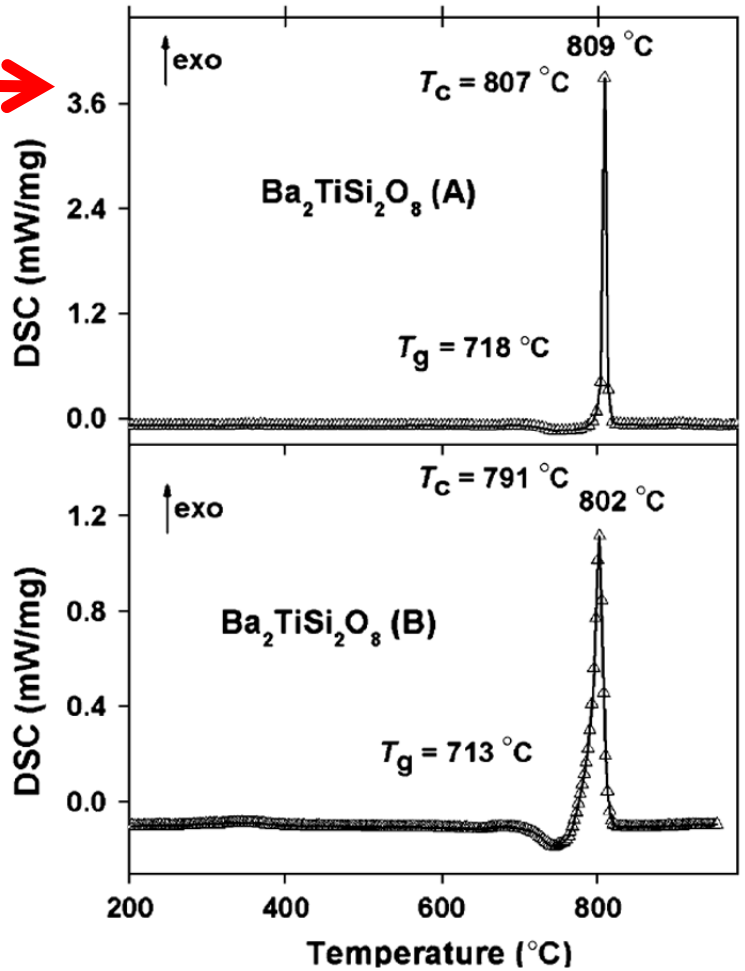
Amorphous component of glass evident in PXRD

Crystallization of Fresnoite ($Ba_2TiSi_2O_8$)

Differential scanning calorimetry reveals that the crystallization rate of the **fresnoite** glasses increased with increasing devitrification.

DSC of $BaTiSiO_5$ glass





DSC of $Ba_2TiSi_2O_8$ glasses (A & B)

T_g = onset glass transition temperature
T_c = onset crystallization temperature

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Enthalpy of Vitrification (ΔH_{vit})

Enthalpy of Vitrification:
fresnoite composition samples from constituent oxides behave exothermic & became more exothermic with increasing crystallinity

	ΔH_{vit} (kJ/mol)	
	reported	**2-oxygen basis**
SiO_2 (cristobalite)[a]	9	9
$CaAl_2Si_2O_8$ (anorthite)[a]	77.8	19.5
$Ba_2TiSi_2O_8$ (fresnoite)	93.8	23.5
$CaTiSiO_5$ (titanite)[b]	80.8	32.3

(a) Navrotsky, A. et al., *Geochim. Cosmochim. Acta* **1980**, *44*, 1409
(b) Xirouchakis, D. et al., *Am. Mineral.* **1997**, *82*, 754

ΔH_{vit} increases with increasing Ti / (Ti + Si), similar to that of aluminosilicates

Fresnoite has a slightly better glass forming ability than Titanite

T.-J. Park, M.J. Davis, P. Vullo, T.M. Nenoff, J. L. Krumhansl, A. Navrotsky. *J. Am. Ceram. Soc.*, **2009**, *92*(9), 2053.

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Solubility Testing, Modified PCT- Procedure B

Product consistency test (PCT-B) tests suggest that both glassy and crystalline fresnoite ($Ba_2TiSi_2O_8$) exhibit favorable aqueous stability for long-term storage

The Modified Product Consistency Test—Procedure B (PCT-B) Results for Fresnoite Glass A and Crystal E

	3 days		10 days	
	FR% (Ba loss)	*NL* (10^{-3}g·(m^{2}d)$^{-1}$)	FR% (Ba loss)	*NL* (10^{-3}g·(m^{2}d)$^{-1}$)
A	0.42	10.07	0.33	2.34
E	0.33	8.26	0.43	3.20

Values are comparable to that of borosilicates (10^{-2}g·(m^{2}d)$^{-1}$)

Enthalpies of Reactions

	enthalpy, kJ
$2BaO + TiO_2 + 2\ SiO_2 = Ba_2TiSi_2O_8$ (fresnoite)	-342.3
$2BaO + TiO_2 + 2SiO_2 = Ba_2TiSi_2O_8$ (glass)	-248.3
$Ba_2TiSi_2O_8$ (fresnoite) = $Ba_2TiSi_2O_8$ (glass)	94.0
$Ba_2TiSi_2O_8$ (fresnoite) = $BaTiO_3 + Ba_2Si_2O_5$	87.1
$Ba_2TiSi_2O_8$ (fresnoite) + $TiO_2 = 2BaTiSiO_5$	148.7
$BaO + TiO_2 = BaTiO_3$ (perovskite)	-152.3
$BaO + 2SiO_2 = BaSi_2O_5$ (sanbornite)	-41.3
$BaO + TiO_2 + SiO_2 = BaTiSiO_5$ (glass)	-127.6

Better stability

Plan to measure heat capacity and calculate entropy of fresnoite, apply to free energy and solubility

9/2/2009

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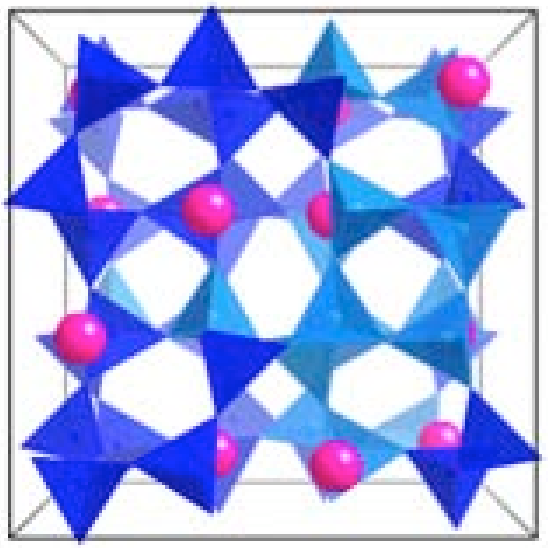
Cs,Ba-Ti-Si-O Pollucite Waste Form Studies

- Ba-substituted $CsTiSi_2O_{6.5}$ (Pollucite Analog) are of interest as durable ceramic waste forms because of their formation from heat treatment of CST Cs-getters.
- Cs,Ba-pollucite samples were prepared by a solid state synthesis.
- Two types were synthesized, $Cs_xBa1_xTiSi_2O_{(7-x/2)}$ and $Cs_xBa_{(1-x)/2}TiSi_2O_{6.5}$ were synthesized with pollucite structure (1>x>6)
- Calorimetry, NMR and Neutron Diffraction is in progress

Tectosilicates
3-D framework
SiO_2 tetrahedra

Feldspathoid group
Pollucite
$CsTiSi_2O_{6.5}$
($CsAlSi_2O_6$)



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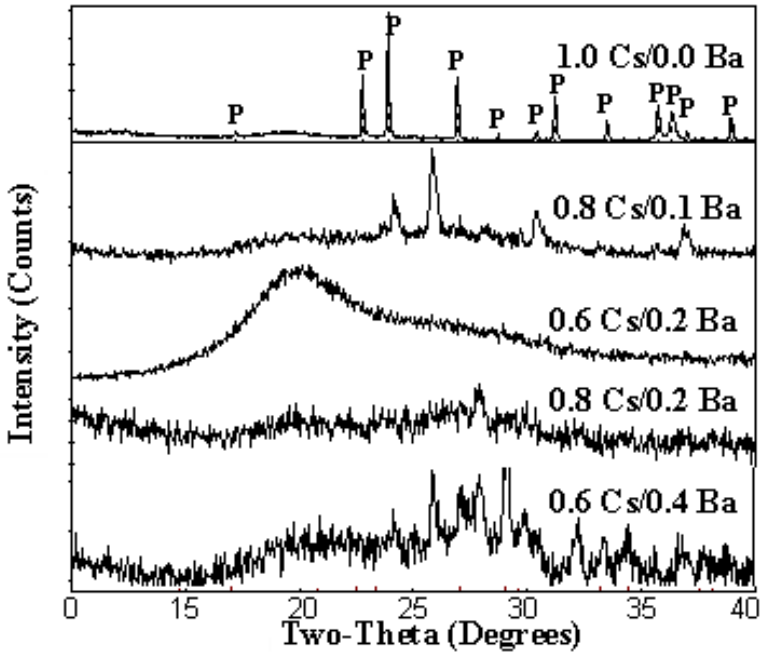
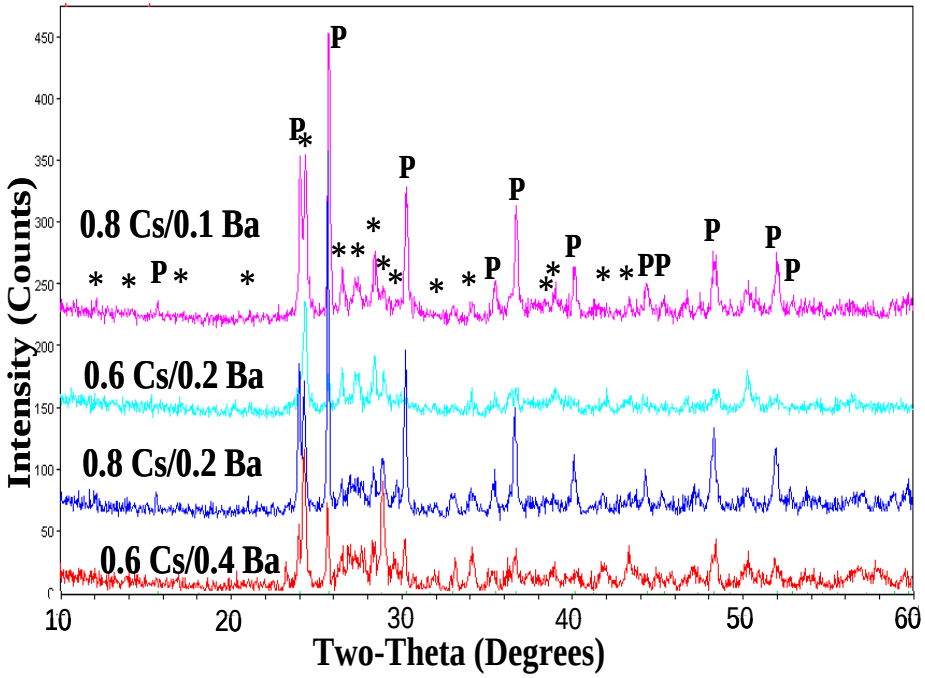
Cs,Ba-Ti-Si-O Pollucite: $Cs_xBa_{(1-x)/2}TiSi_2O_{6.5}$

Ba-substituted $CsTiSi_2O_{6.5}$ with the pollucite structure were synthesized using $CsTiSi_2O_{6.5}$ seed crystals in a wide variety of stoichiometries

no seed crystals



with 10% seed crystals



T. Garino, T.M. Nenoff, T.-J. Park, A. Navrotsky. *J. Am. Ceram. Soc.* **2009**, *92*(9), 2144.

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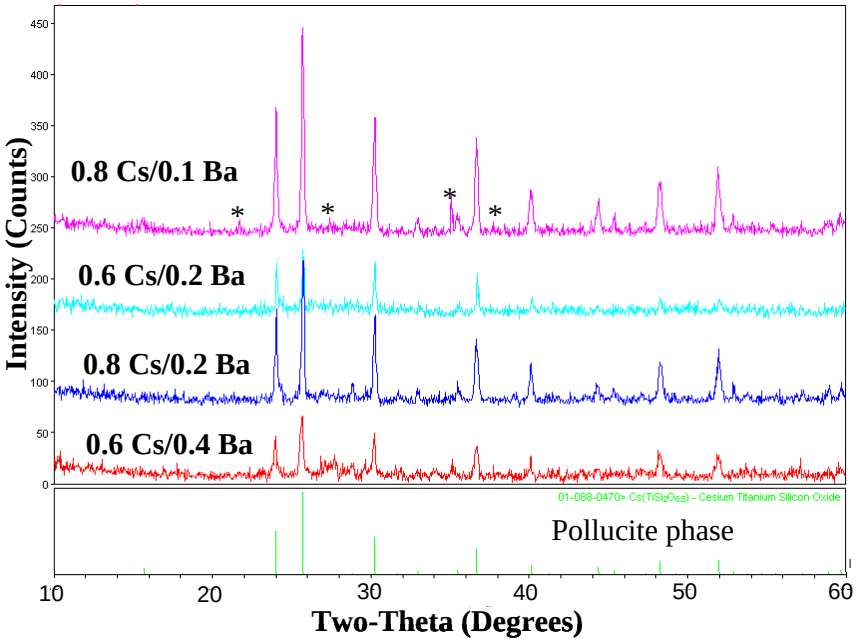
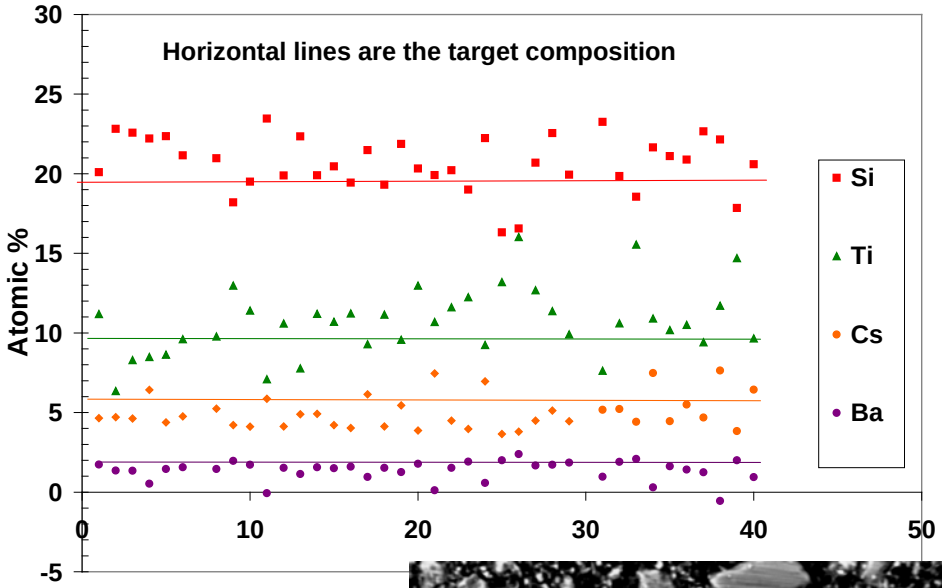
Cs,Ba-Ti-Si-O Pollucite: $Cs_xBa_{(1-x)/2}TiSi_2O_{6.5}$

Optimized crystallization temperature was determined to be 750˚C, resulting in *enhanced phase purity*

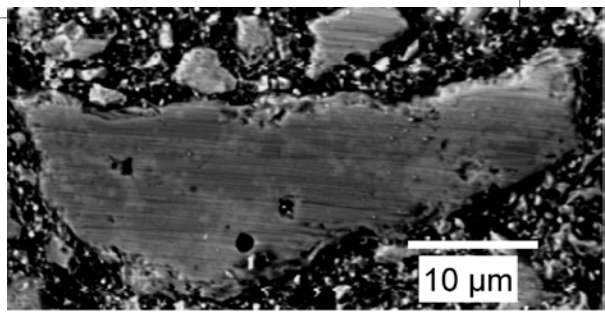
Microprobe Analysis: Ba is incorporated in the pollucite structure.





750°C, 20 hr with 10% seeds

Flat region sampled by microprobe



T.M.Nenoff, tmnenof@sandia.gov

Conclusions

Pollucite Samples:

Perform calorimetry and x-ray/neutron diffraction studies on samples of $Cs_{0.9}Ba_{0.05}TiSi_2O_{6.5}$, $Cs_{0.8}Ba_{0.1}TiSi_2O_{6.5}$, $Cs_{0.7}Ba_{0.15}TiSi_2O_{6.5}$, $Cs_{0.6}Ba_{0.2}TiSi_2O_{6.5}$

Synthesize $Cs_{(1-x)}Ba_xTiSi_2O_{6.5+x/2}$ powders using seed method and perform calorimetry and diffraction studies on them.

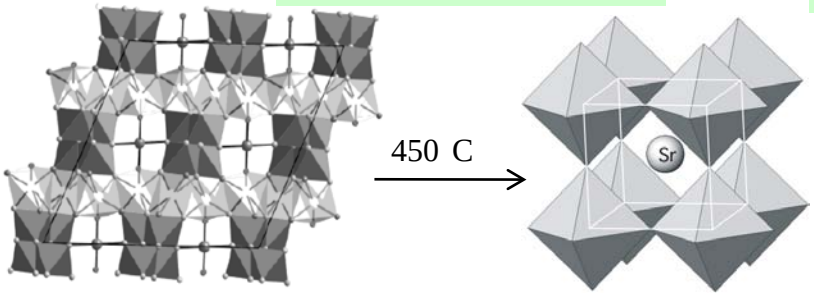
Compare stability predictions between Titanite, Fresnoite, Pollucite Titanosilicates

Future Research Areas:

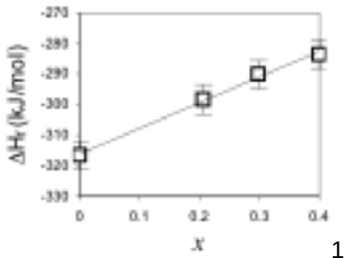
SOMS Niobate Molecular Sieves heat treat to Perovskite waste form structures.

Study of Waste Form stability versus cation oxidation state for series of **$Sr^{2+} \rightarrow Y^{3+} \rightarrow Zr^{4+}$**

SOMS → $SrNb_{2-x}Ti_xO_{6-0.5x}$



Enthalpies of formation for $Na_2Nb_{2-x}Ti_xO_{6-0.5x}$



J. Mater. Res., **2005,** 20(3), 618
JACS., **2002**, 124(3), 1704.

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Acknowledgement

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Thermochemical Cycle for Formation of $Ba_2TiSi_2O_8$

Standard molar enthalpies of formation ($\Delta H^o_{f,ox}$) from the constituent oxides

$2BaO\ (soln, 701\ ^oC) + TiO_2\ (soln, 701\ ^oC) + 2SiO_2\ (soln, 701\ ^oC) \rightarrow Ba_2TiSi_2O_8\ (solid, 701\ ^oC)$ (1)

$2BaO\ (solid, 25\ ^oC) \rightarrow 2BaO\ (soln, 701\ ^oC)$ (2)

$TiO_2\ (solid, 25\ ^oC) \rightarrow TiO_2\ (soln, 701\ ^oC)$ (3)

$2SiO_2\ (solid, 25\ ^oC) \rightarrow 2SiO_2\ (soln, 701\ ^oC)$ (4)

$2BaO\ (solid, 25\ ^oC) + TiO_2\ (solid, 25\ ^oC) + 2SiO_2\ (solid, 25\ ^oC) \rightarrow Ba_2TiSi_2O_8\ (solid, 25\ ^oC)$ (5)

$\Delta H^o_{f,ox}\ (fresnoite, \Delta H(5)) = \sum \Delta H(i)\ (i = 1 - 4)$