Use of high-temperature oxide melt solution calorimetry in understanding long-term behaviors of ceramic waste forms

제16회 한국원자력학회 춘계학술대회
2016년 5월 11-13일

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한국원자력연구원
Korea Atomic Energy Research Institute

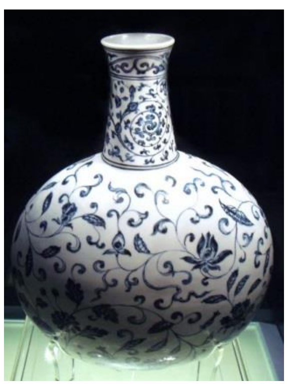
Ceramics

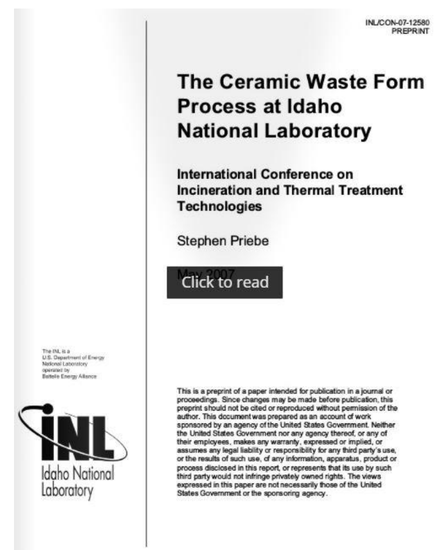
An inorganic, nonmetallic solid material

Crystallinity: Glass → Ceramic

Application:

pottery, tableware, cookware, building materials, aerospace materials, to nuclear materials (e.g., UO_2 pellets, waste forms, etc.)





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PREPRINT

The Ceramic Waste Form Process at Idaho National Laboratory

International Conference on Incineration and Thermal Treatment Technologies

Stephen Priebe

May 2007

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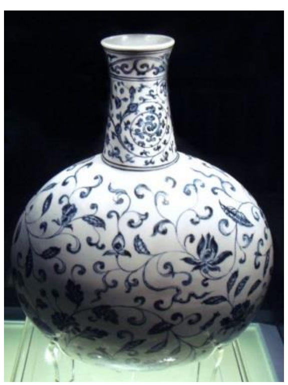
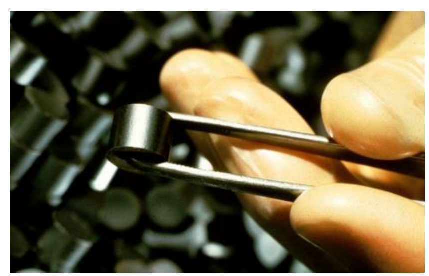
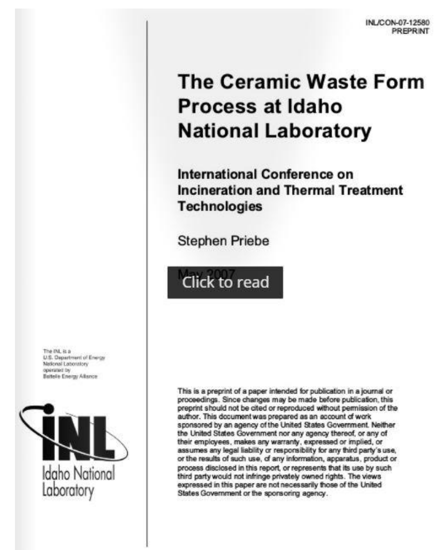
waste forms → "$A_aB_bC_cO_x$"







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Ceramic Waste Forms

$$A_aB_bC_cO_x \quad vs. \quad A'_{a'}B'_{b'}C'_{c'}O_x$$

$A_aB_bC_cO_x$ vs. $A'_{a'}B'_{b'}C'_{c'}O_x$

Which one is better?

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Durability, Stability

Ceramic Waste Forms

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Which one is better? **Durability, Stability**

Which one is more stable?

$A_aB_bC_cO_x$ vs. $A'_{a'}B'_{b'}C'_{c'}O_x$

Which one is better? Durability, Stability

Which one is more stable? Thermodynamics

	Enthalpy, kJ/mol
$2SrO + TiO_2 + 2SiO_2 \rightarrow Sr_2TiSi_2O_8$ (fresnoite)	-246.8
$2SrO + TiO_2 + 2SiO_2 \rightarrow Sr_2TiSi_2O_8$ (glass)	-178.3

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Long-term behaviors?

Ceramic Waste Forms

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Long-term behaviors? Thermochemistry

	Enthalpy, kJ/mol
$Sr_2TiSi_2O_8$ (fresnoite) + $TiO_2 \rightarrow 2SrTiSiO_5$ (glass)	70.6
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$A_aB_bC_cO_x$ vs. $A'_{a'}B'_{b'}C'_{c'}O_x$

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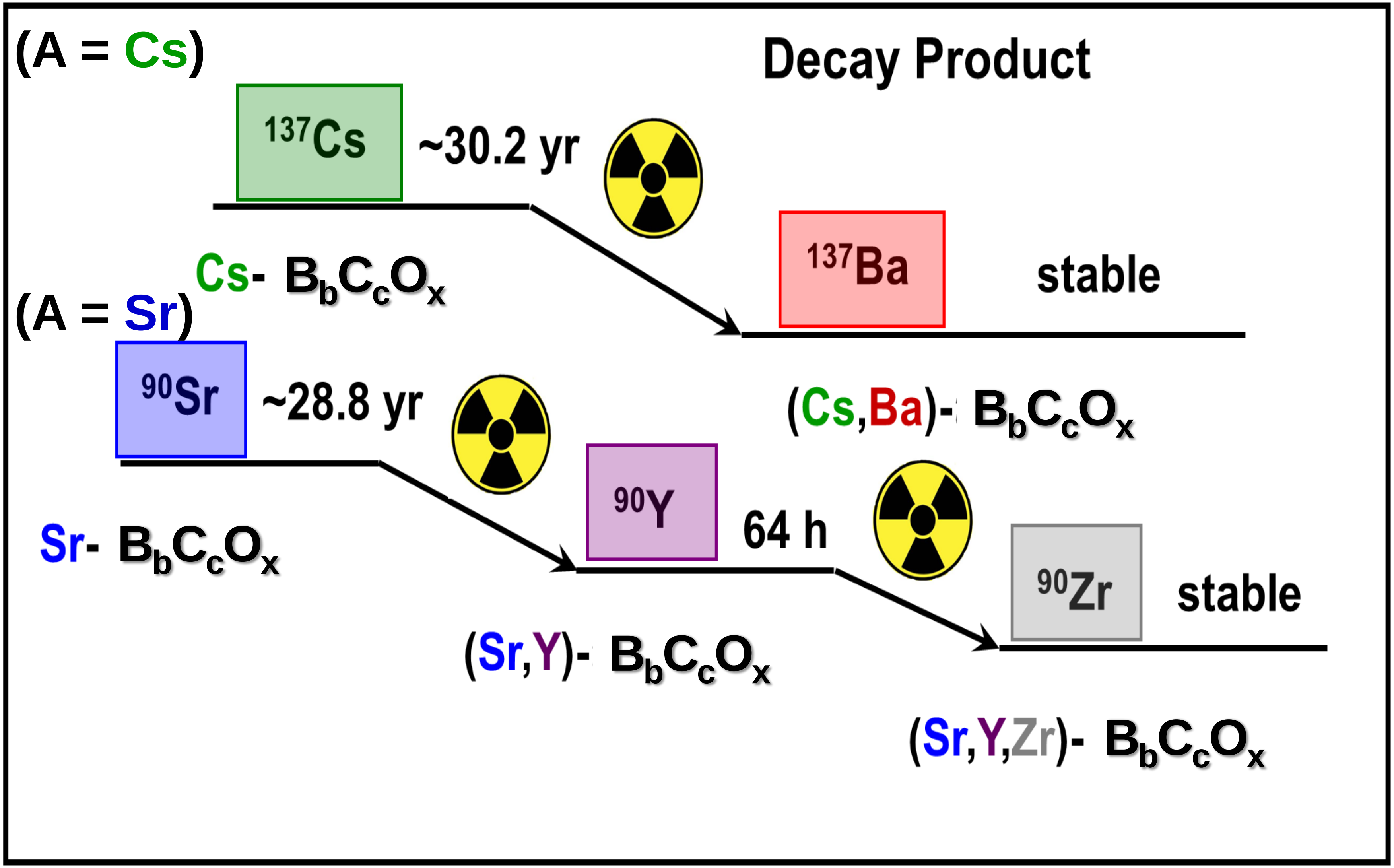
DECAY EFFECT?

Decay Product Stability

$A_aB_bC_cO_x$



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$CsB_bC_cO_x \rightarrow Cs_{0.5}Ba_{0.25}\square_{0.25}B_bC_cO_x$

$\rightarrow Cs_{0.25}Ba_{0.375}\square_{0.375}B_bC_cO_x \rightarrow\rightarrow \ldots$

In nature, charge is balanced

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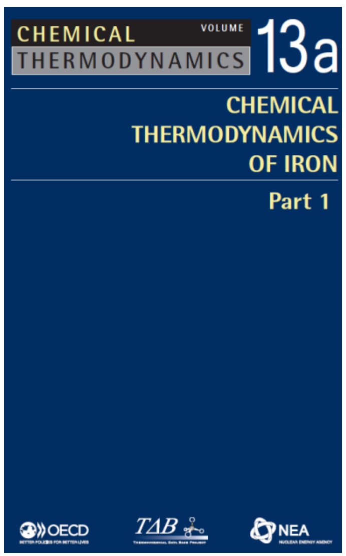
$\rightarrow Cs_{0.25}Ba_{0.375}\square_{0.375}B_bC_cO_x \rightarrow\rightarrow \ldots$

HOW DO THE STRUCTURE AND ITS STABILITY RESPOND TO THESE CHANGES?

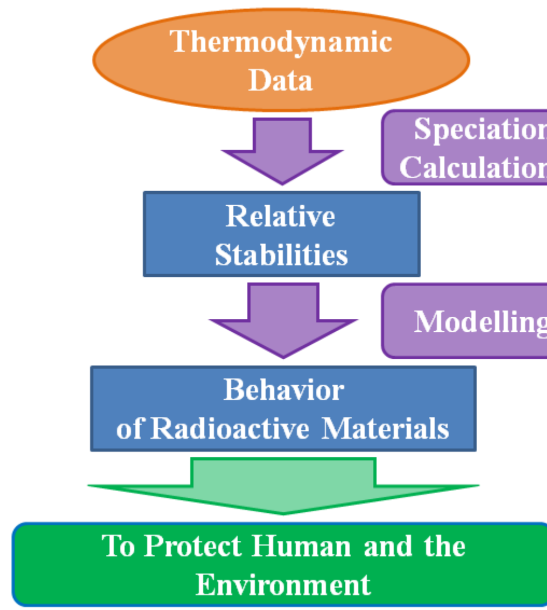
열역학정보(예: 형성엔탈피 등) 구축

- 원자력연료/폐기물 등의 열역학적 안정성을 예측하고 거동특성을 평가하는데 반드시 필요함

- 원자력 분야 뿐 아니라 에너지, 환경, 재료, 나노, 화학 등 다양한 분야에 활용되는 기초 정보임

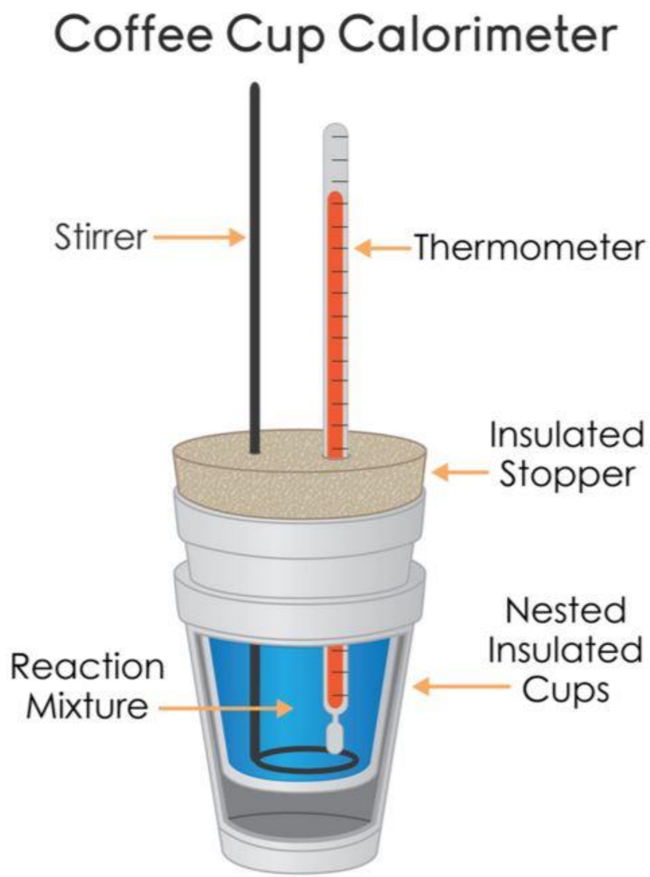


OECD NEA:
Chemical Thermodynamics



열량계

- 열량을 측정하는 계기. 칼로리미터 (Calorimeter)
- A calorimeter is a device used to measure the quantity of heat transferred to or from an object.



기술장벽

- 원자력연료/폐기물 등은 대부분 고체상으로 존재
  (암석, 광물, 세라믹 물질 등)

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수용액에 녹지 않는 고체

→ 기존의 방법(다른 열량계)으로 형성엔탈피 등을 구할 수 없음

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Metal Oxides (including $A_aB_bC_cO_x$)

→ 용융염 조건에서 녹일 수 있음

→ 따라서, 형성엔탈피 등을 구할 수 있음

고온용융염 칼로리미터

- <u>High Temperature Oxide Melt Solution Calorimetry:</u>
  용융염 조건에서 열역학 정보를 측정할 수 있는 시스템

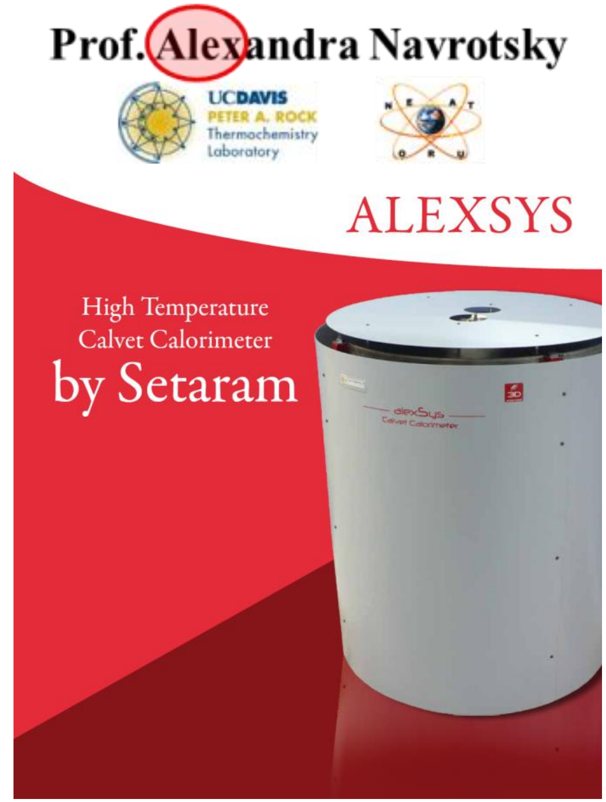
- 세계적으로 미국, 독일, 러시아, 인도만 소유 중임.

미국: <u>UC Davis (원천기술개발)</u>,
Pacific Northwest National Laboratory,
Los Alamos National Security, LLC,
Univ of Notre Dame

독일: Freiburg University,
Karlsruhe Institute of Technology (KIT)

러시아: National Univ. of Science and Technology

인도: BARC – Actinide Thermochemistry Section

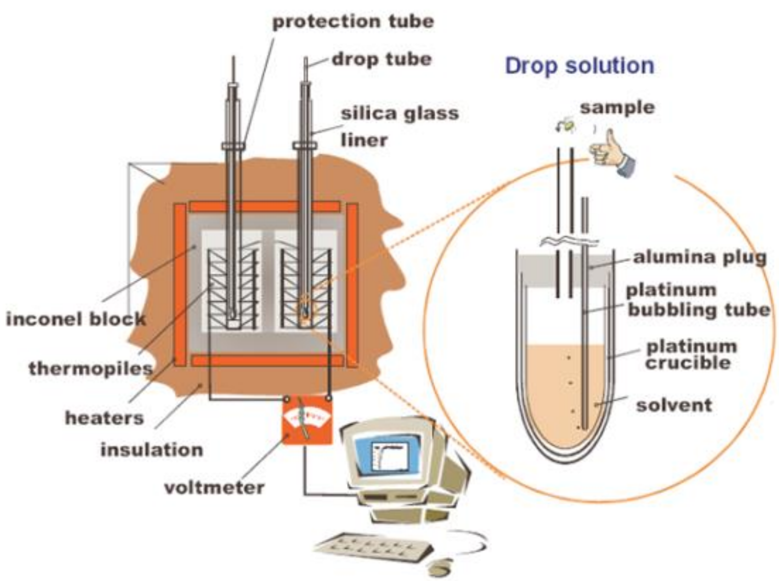


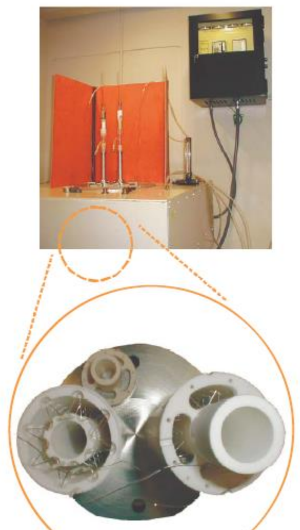
고온용융염 칼로리미터 장비 원리

- 시료가 상온에서 고온에 이르기까지의 열(ΔH_{ttd})과 용해시 발생하는 열(ΔH_{sol})의 합(ΔH_{ds})을 측정

• $\Delta H_{ds} = \Delta H_{ttd} + \Delta H_{sol}$

• $\Delta H_{ttd} = \int_{25C}^{702C} C_p dT$





Thermopiles with inconel block removed, as viewed from the top

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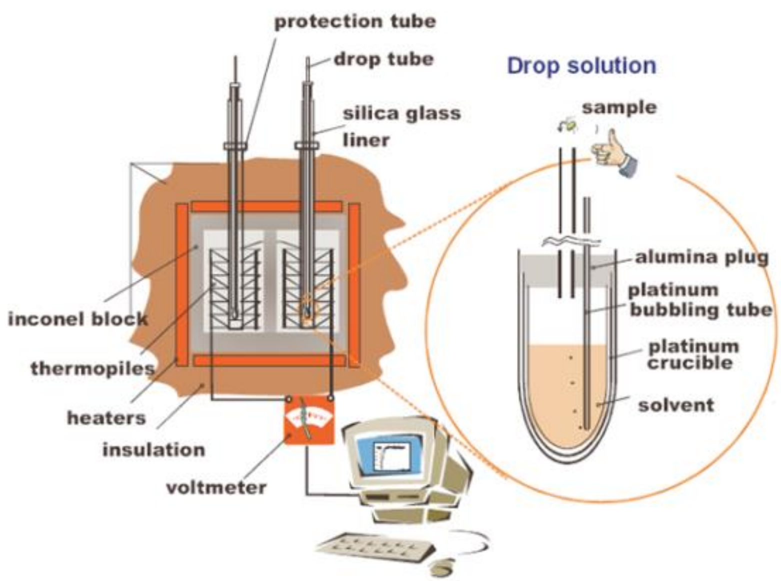
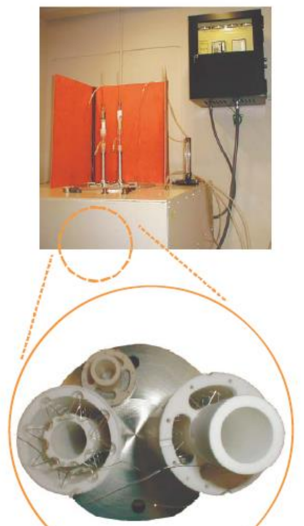



Thermopiles with inconel block
removed, as viewed from the top

- Thermochemical cycle을 적용하여 형성엔탈피($\Delta H_{f,ox}$) 계산

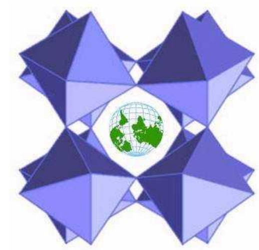
Thermochemical Cycles – Perovskites (ABO_3)

ABO_3 (solid, 25°C) → ABO_3 (dissolved, 702°C) (1)

(ABO_3 (dissolved, 702°C) = AO (dissolved, 702°C) + BO_2 (dissolved, 702°C))

AO (solid, 25°C) → AO (dissolved, 702°C) (2)
BO_2 (solid, 25°C) → BO_2 (dissolved, 702°C) (3)

AO (solid, 25°C) + BO_2 (solid, 25°C) → ABO_3 (solid, 25°C) (4)



$\Delta H(4) = \Delta H^{o}_{f,ox}(ABO_3) = \Delta H(2) + \Delta H(3) - \Delta H(1)$

$\Delta H(1) = \Delta H_{ds}(ABO_3)$; $\Delta H(2) = \Delta H_{ds}(AO)$; $\Delta H(3) = \Delta H_{ds}(BO_2)$

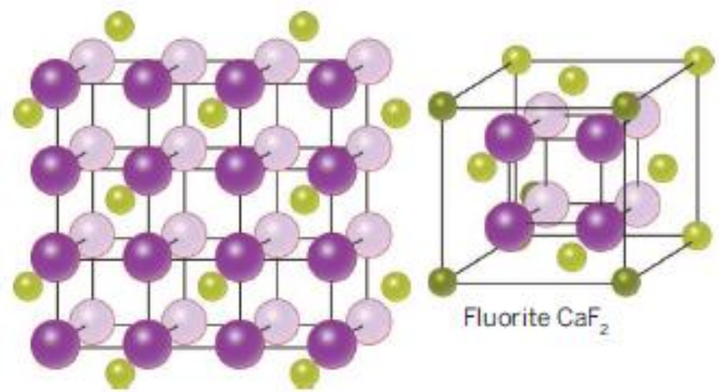
적용분야

- 관심물질의 안정성 예측 및 거동특성 평가

	Enthalpy, kJ/mol
$Sr_2TiSi_2O_8$ (fresnoite) + TiO_2 $\rightarrow$ $2SrTiSiO_5$ (glass)	70.6
$Sr_2TiSi_2O_8$ (glass) + TiO_2 $\rightarrow$ $2SrTiSiO_5$ (glass)	-7.9

US DOE NERI project (DE-FC07-07ID14830): *Development of New Fission Products*

"Nuclear Fuel in a Reactor Accident," *Science* 335, 1184 (2012).



"Taking the Measure of Molten Uranium Oxide," *Science* 346, 916 (2014).

US DOE Nuclear Energy Research Initiative (NERI):

New Fission Product Waste Forms: Development and Characterization

<u>*Neosilicates*</u>

Orthosilicates

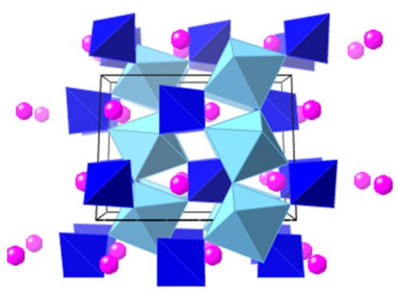
Isolated $[SiO_4]^{4-}$

Titanite (sphene)

$CaTiSiO_5$

$SrTiSiO_5$

$BaTiSiO_5$



<u>*Sorosilicates*</u>

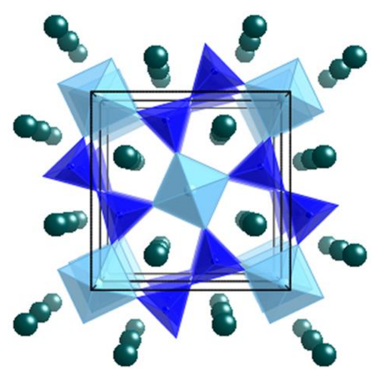
Isolated double tetrahedra $[Si_2O_7]^{6-}$

Melilite group

Fresnoite

$Ba_2TiSi_2O_8$

$Sr_2TiSi_2O_8$



<u>*Tectosilicates*</u>

3-D framework

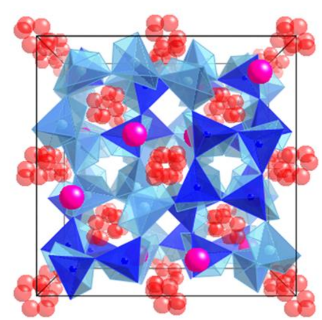
SiO_2 tetrahedra

Feldspathoid group

Pollucite

$CsTiSi_2O_{6.5}$

$(CsAlSi_2O_6)$



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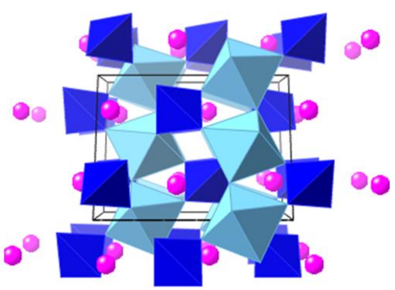

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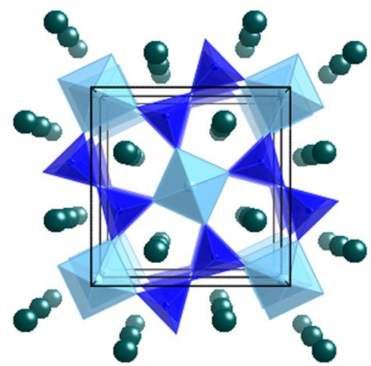

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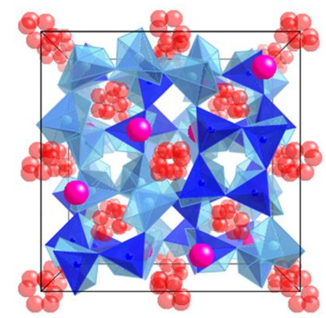
3-D framework
SiO_2 tetrahedra

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



Pollucite

$CsAlSi_2O_6$ → $CsTiSi_2O_{6.5}$ (Titanosilicates)

named after Pollux

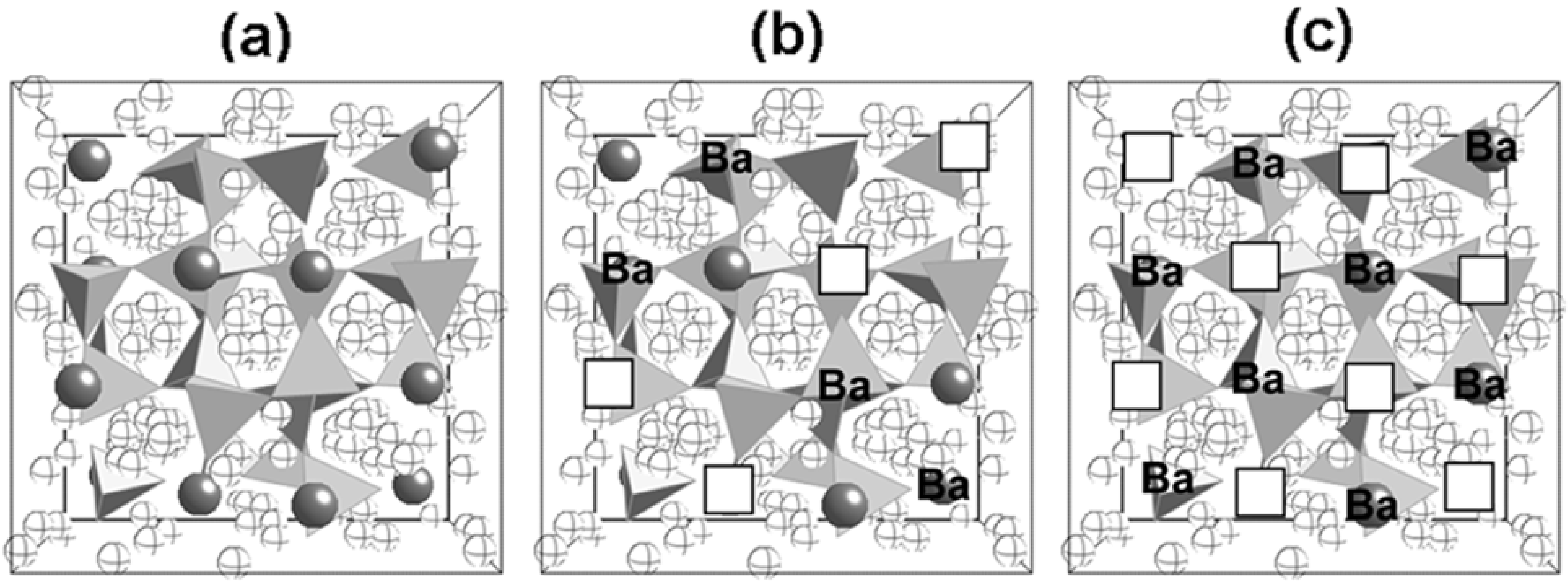
wikipedia.com

Attribution: Janos Korom Dr.

Decay Scheme (1)

(1) Charge-balanced route: $2Cs^{1+} = Ba^{2+}$ + vacancy

$CsTiSi_2O_{6.5}$ (a) → $Cs_{0.5}Ba_{0.25}\square_{0.25}TiSi_2O_{6.5}$ (b) →
(Pollucite)
→→ $Ba_{0.5}\square_{0.5}TiSi_2O_{6.5}$ (c)



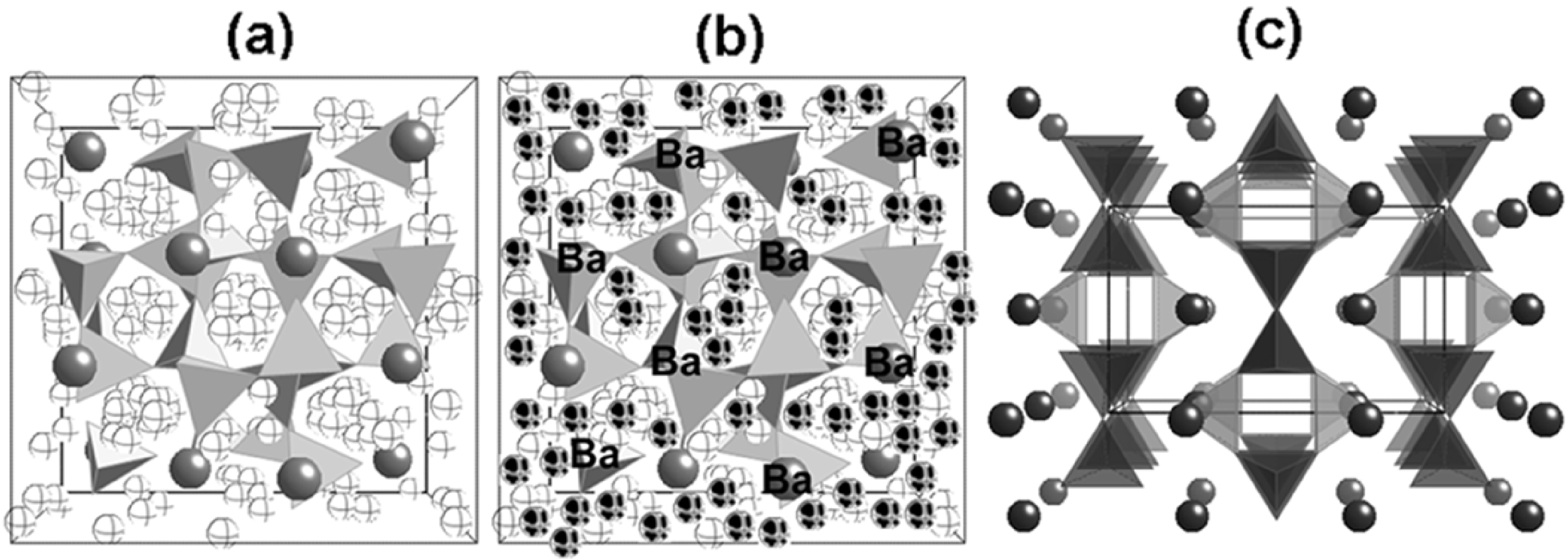
Decay Scheme (2)

(2) 1:1 replacement of Cs by Ba

$CsTiSi_2O_{6.5}$ (a) → $Cs_{0.5}Ba_{0.5}TiSi_2O_{6.75}$ (b) →

→→ ~~$BaTiSi_2O_{6.5}$~~ (This pollucite does not exist)

→→ $BaTiSi_2O_7$ (c)



Thermochemical Data and Cycle

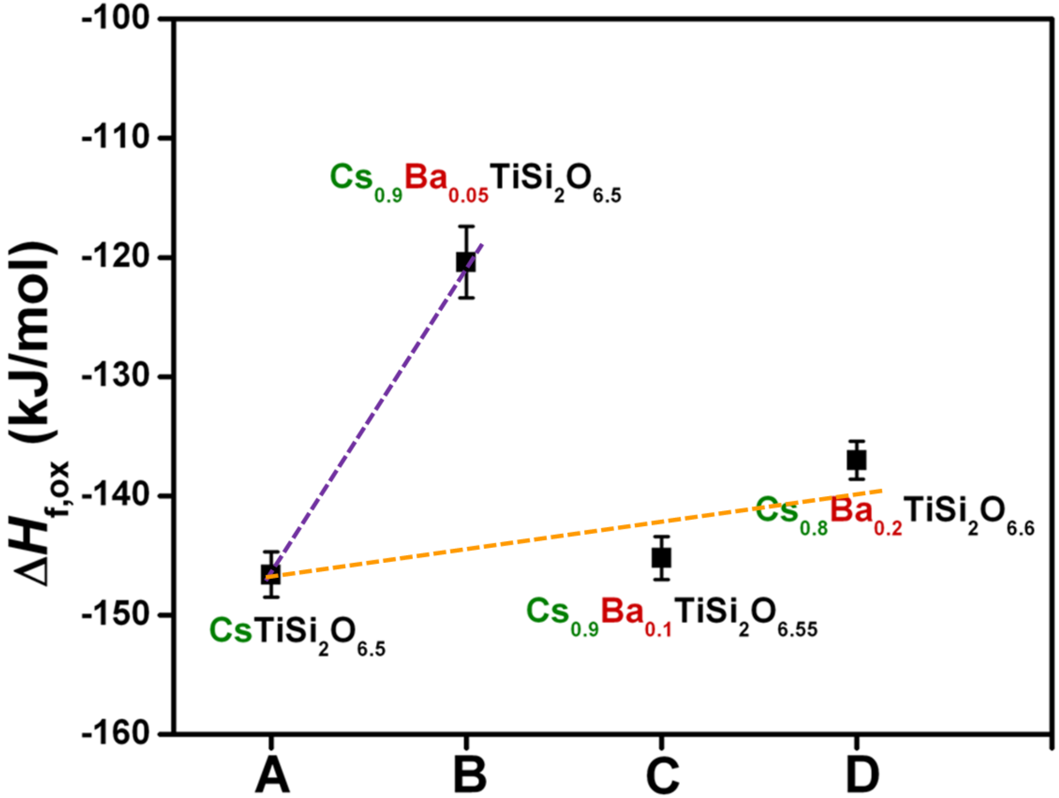
	ΔH_{ds} (J/g)	ΔH_{ds} (kJ/mol)	$\Delta H^0_{f,\ ox}$ (kJ/mol)	$\Delta H^0_{f,\ el}$ (kJ/mol)
(A) $CsTiSi_2O_{6.5}$	552.3 ± 4.8	188.3 ± 1.7	-146.3 ± 2.2	-3084.7 ± 3.2
(B) $Cs_{0.9}Ba_{0.05}TiSi_2O_{6.5}$	500.1 ± 7.9	166.9 ± 2.6	-120.4 ± 3.0	-3068.9 ± 3.7
(C) $Cs_{0.9}Ba_{0.1}TiSi_2O_{6.55}$	547.1 ± 3.0	187.2 ± 1.0	-145.2 ± 1.8	-3121.1 ± 2.9
(D) $Cs_{0.8}Ba_{0.2}TiSi_2O_{6.6}$	521.2 ± 3.8	179.0 ± 1.3	-137.0 ± 1.6	-3150.4 ± 2.0
Cs_2O	—	-183.3 ± 1.4[17]	—	-346.0 ± 1.2[20]
BaO	—	-91.5 ± 1.9[18]	—	-548.1 ± 2.1[20]
TiO_2	—	55.4 ± 1.2[19]	—	-944.0 ± 0.8[20]
SiO_2	—	39.1 ± 0.3[18]	—	-910.7 ± 1.0[20]

Uncertainty is two standard deviations of the mean.

	Reaction	Enthalpy
1	$CsTiSi_2O_{6.5}$ (solid, 25 °C) → $CsTiSi_2O_{6.5}$ (dissolved, 702 °C)	$\Delta H_1 = \Delta H_{ds}$ (sample)
2	Cs_2O (solid, 25 °C) → Cs_2O (dissolved, 702 °C)	$\Delta H_2 = \Delta H_{ds}$ (Cs_2O)
3	TiO_2 (solid, 25 °C) → TiO_2 (dissolved, 702 °C)	$\Delta H_3 = \Delta H_{ds}$ (TiO_2)
4	SiO_2 (solid, 25 °C) → SiO_2 (dissolved, 702 °C)	$\Delta H_4 = \Delta H_{ds}$ (SiO_2)
5	$0.5Cs_2O$ (solid, 25 °C) + TiO_2 (solid, 25 °C) + SiO_2 (solid, 25 °C) → $CsTiSi_2O_{6.5}$ (solid, 25 °C)	$\Delta H_5 = \Delta H_{f,ox}$ (sample) $= \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_1$

Park, T.-J. *et al.*, *J. Am. Ceram. Soc.* **94**[9], 3053 (2011).

Summary



$\Delta H_{f,ox}$ are exothermic and become less so with increasing Ba content.

The effect of vacancies **in the pollucite structure is a more dominant factor in the energetics than** ***that of Ba replacement*****.**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