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# Synthesis and Characterization of Silicon Clathrates for Anode Applications in Lithium-Ion Batteries

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**Project ES149**



BERKELEY LAB

BATT Batteries for Advanced Transportation Technologies

U.S. DEPARTMENT OF ENERGY

# Overview

## Timeline

- Program Start: January 2011
- Program End: December 2014

## Budget

- DOE Share: $1.15M
- Funding Received in FY11: $299k
- Funding for FY12: $149k

## Barriers

- (A) - Cost
- (C) - Performance
- (E) - Life

## Targets

| Specific Energy (W·h/kg) | Specific Power (W/kg) | Cycle-Life | Calendar Life (yr) |
|---|---|---|---|
| 200 (EV) | 316 | 1000 | 15 |
| 96 (PHEV) | 316 | 3000 (40 mi equiv.) | 15 |

**Baseline Systems: Conoco Phillips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)**

## Collaborators

- Arizona State Univ. (Candace Chan)
- Florida International Univ. (Jiuhua Chen)

# *Objectives - Relevance*

<u>Overall</u>

- Theoretically and experimentally assess the intrinsic physicochemical, mechanical and electronic advantages of Type I silicon clathrate ($Si_{46}$) over conventional (diamond) silicon ($Si_4$) as a high-performance anode material for $Li^+$ batteries
- Demonstrate improved life and abuse tolerance of $Li^+$ batteries using $Si_{46}$ and its metal-silicon analogues as anode materials

<u>Current</u>

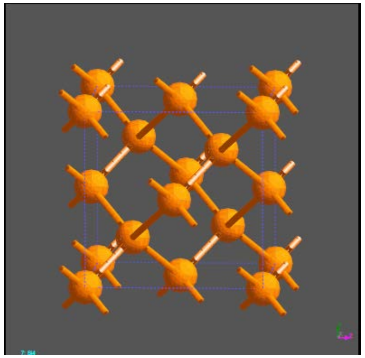
- Employ first principles methods to engineer silicon clathrate compositions that exhibit small volume expansion/contraction, and high specific energy density, while avoiding capacity fading in comparison with conventional $Si_4$
- Synthesize and characterize Type I silicon clathrates ($Si_{46}$) and Type I metal-silicon clathrate alloys ($M_xSi_{46-x}$) – either empty or containing guest atoms
- Formulate and prepare silicon clathrate-based anode electrodes and assemble electrochemical half-cells for measurement of cyclic capacity

# *Milestones*

| Target Date | Milestone | Status |
|---|---|---|
| 06/2011 | Prepare 1-2 gram quantities of Type I silicon clathrates by one or more synthesis methods | Complete |
| 09/2011 | Select one or two synthetic pathways for further development | Complete |
| 09/2011 | Identify possible reaction pathways (based on modeling results) for the formation of empty clathrates $Si_{46}$, $Li_xSi_{46}$, and $Li_{15}Si_4$ | Complete |
| 09/2011 | Construct and evaluate an electrochemical half-cells using clathrate materials synthesized in Year 1 | Complete |
| 03/2012 | Predict the $Li^+$ occupancy and lattice expansion potential of Type I metal-silicon clathrate alloys using classical and *ab initio* calculations | Complete |
| 06/2012 | Continue identifying possible reaction pathways for the formation of empty clathrates □$Si_{46}$, $Li_xSi_{46}$, $Li_{15}Si_4$, and $Li_xM_ySi_{46-y}$ | Pending |
| 09/2012 | Synthesize hundreds of grams of Type I silicon clathrates and/or metal-silicon Type I clathrate alloys with complementary determination of structural purity | Pending |

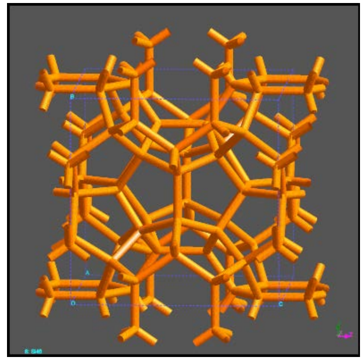
# *Strategy*

*Asses the structural and electronic attributes of Type I clathrate $Si_{46}$ versus conventional $Si_4$*

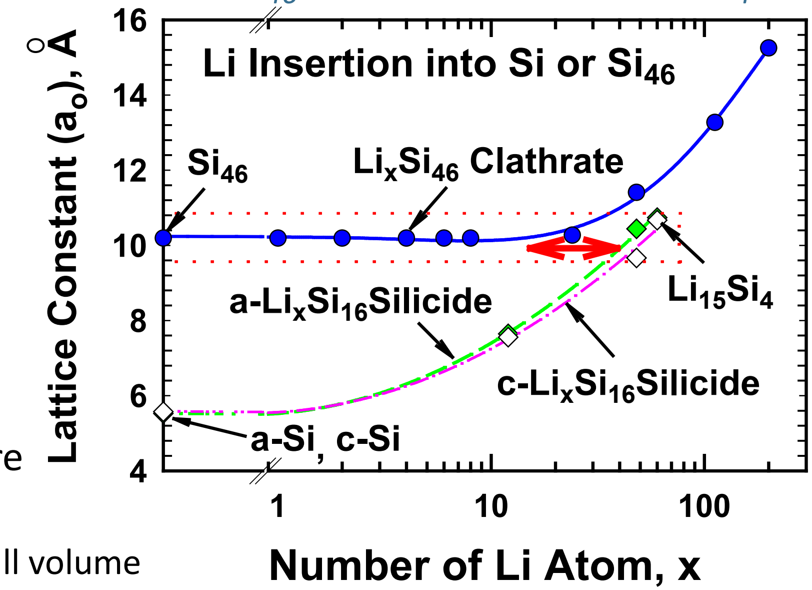


$Si_4$ $[Fd\bar{3}m]$
Diamond Structure

Allotropic Transformation



$Si_{46}$ $[Pm\bar{3}n]$
Clathrate Type I Structure




- Undergoes large volume changes (> 300%) on charging/discharging
- Mechanically unstable
- Capacity loss

- Computations indicate small volume change in $Si_{46}$ compared to a-Si or c-Si
- $Li_xSi_{46}$ and $Li_{15}Si_4$ have similar lattice constants
- Specific grav. capacity of 478 mA·h/g

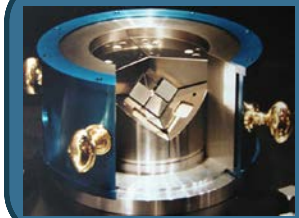
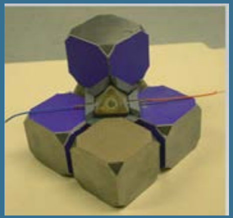
Validate theoretical predictions by synthesizing silicon clathrates and measuring electrochemical capacity

| Structure | Space Group | Lattice Constant (Å) | Predicted Equilibrium Volumes (Å³/u.c.) | | | | No of Li⁺ | Specific Grav. Capacity (mA·h/g) |
|---|---|---|---|---|---|---|---|---|
| | | | Total Cell | Available | Occupiable | Accessible | | |
| $Si_{46}$ (Type I) | $Pm\bar{3}n$ | 10.355 | 1110 | 169.51 | 47.76 | 43 | 23 | 478 |
| $Si_4$ (diamond) | $Fd\bar{3}m$ | 5.456 | 1191 | 549.9 | 112.83 | 110 | 15 | 4000 |
| C (graph) | $P6_3/mmc$ | 2.460 | 35.64 | 4.25 | 1.89 | 0.78 | 1 | 372 |

# *Approach*

## *Experiment*

**Synthesis of $Si_{46}$ and $M_xSi_{46-x}$ via parallel paths:**

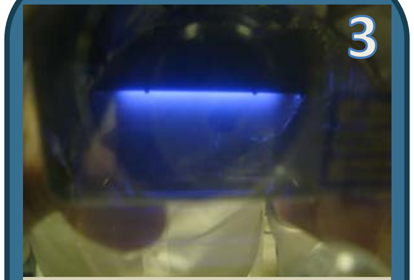



1

High pressure and temperature multi-anvil techniques (high energy)

2

Vacuum arc melting from elemental powders to form $M_xSi_{46-x}$



3

Vacuum PEMS in ionic liquid (IL)

Heterogeneous batch synthesis in solution via Hofmann-type elimination-oxidation reaction

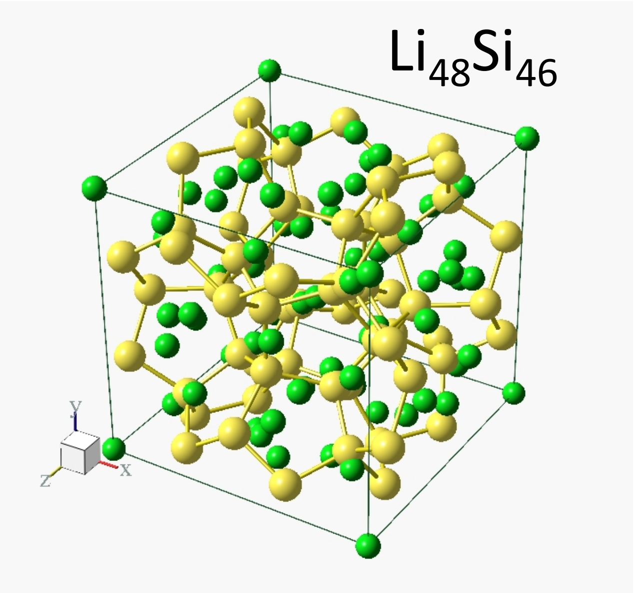
4

$$4[R'\text{-}CH_2\text{-}NR_3]^+ + X_9^{4-} \xrightarrow{\sim 300^\circ C} 9X^0\ [\text{Clathrate I}] + 4[R'{=}CH_2] + 4NR_3 + 2H_2$$

## *Theory*

**First principles predictions of:**

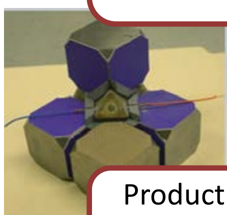
- **Lithiation pathways**
- **Thermodynamic and kinetic constraints**
- **Transformation of allotropic states**
- **Mechanical stability**



# Overview of Accomplishments - Synthesis

## Multi-Anvil High-Pressure & Temp. ✗

**Batch 1 (~30 mg)**
3, 4, 5 GPa
$23BaSi_2 \rightarrow Ba_8Si_{46} + 15Ba$



Product Confirmed by PXRD
h-BN Contamination

**Batch 2 (~1g) Underway**
5 GPa
$8BaSi_2 + 30\ d\text{-}Si \rightarrow Ba_8Si_{46}$

**Completed: Low yield of structural transformation when $BaSi_2$ is employed.**

## Solution Synthesis of {ɩпс ✓

**Trial 1**
$BaSi_2$ + 1B3MI-HFP →
No Yield, IL Decomposed

**Trial 2**
$BaSi_2$ + Proprietary IL →
No Transformation

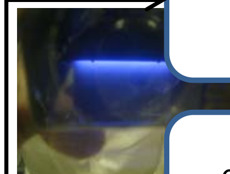
**Trial 3**
$BaSi_2$ + DTMAC-$AlCl_4^-$ →
Partial Transformation to $Si_{46}$, IL Decomposition

**Trial 4**
$BaSi_2$ + DTMAC-BTFMSI →
Transformation to {ɩпс 2Ⲛ $Si_{136}$, No Decomposition of IL

**Trial 5 – Scale-Up (~0.5 g)**
$BaSi_2$ + DTMAC-BTFMSI →
Transformation to $Si_{46}$

**Completed: Product confirmed by PXRD and Raman; removed byproducts; performed EC measurements; yield may be improved with NaSi.**

## Plasma Mag. Synthesis of $Si_{46}$ in IL ✗



**Trial 1**
*d*-Si + 1B3MI-HFP →
Low Yield, Raman Evidence of $Si_{46}$

**Trial 2**
*d*-Si + Castor Oil →
~10 mg Yield, Raman Evidence of $Si_{46}$

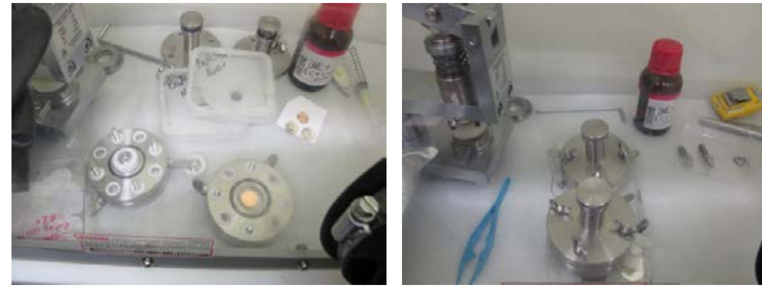
**Prepared Electrode**

**Trial 3**
*d*-Si + Proprietary IL →
Yield of Unknown Particle Size

**Completed: Raman evidence of □$Si_{46}$; particles isolated and imaged; low product yield.**

✓ **= Selected for further development**

# *Overview of Accomplishments – Synthesis (Cont.)*



*Two- and three-electrode electrochemical test cells*

**Vacuum Arc-Melting Synthesis of $M_xSi_{46-x}$ Alloys**

**Trial 1**
38 *d*-Si + 8 Al → $Al_8Si_{38}$

**Trial 2**
38 *d*-Si + 8 Al → $Al_xSi_{38}$

**Trial 3**
38 *d*-Si + 8 Al + 8 Ba → $Ba_8Al_8Si_{38}$

**Trial 4**
38 *d*-Si + 8 Al + 8 Ba → $Ba_8Al_8Si_{38}$

**Trial 5**
38 *d*-Si + 8 Cu + 8 Ba → $Ba_8Cu_8Si_{38}$

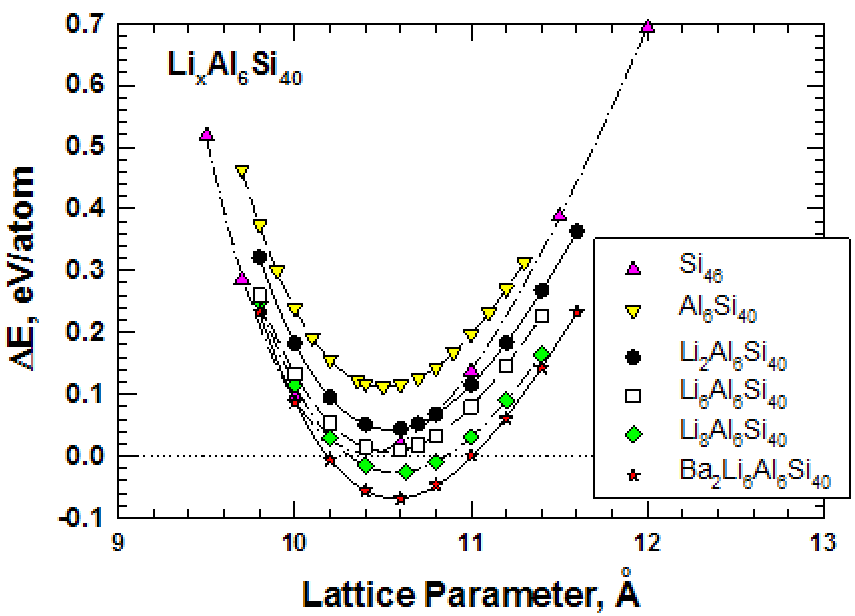
**Trial 6**
38 *d*-Si + 8 Cu + 8 Ba → $Ba_8Cu_8Si_{38}$

**Completed: Products confirmed by PXRD and Raman; performed EC measurements at two labs; high structural purity; some chemical impurities remain; high yield technique.**

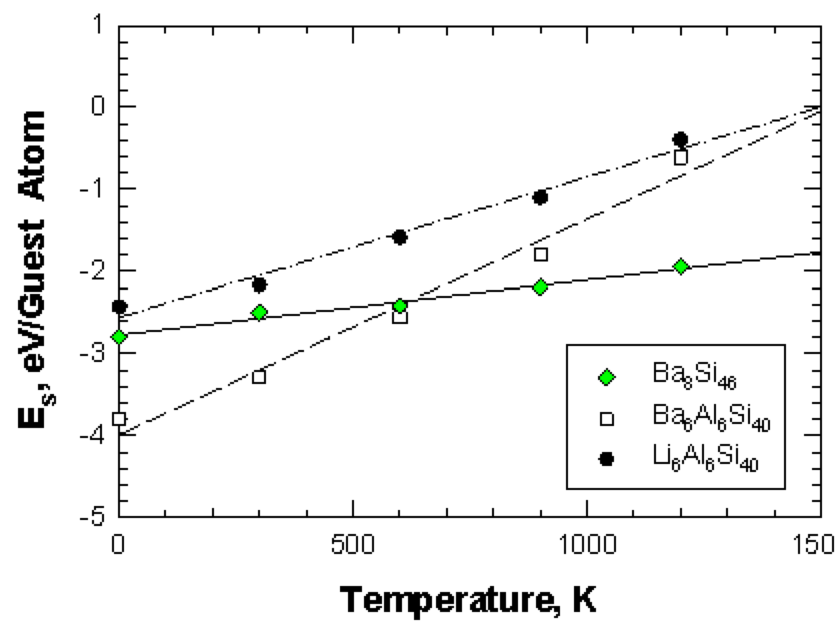
# *Overview of Accomplishments - Computations*

- Computed energies of formation and stabilization using DFT and CPMD for various Type I clathrate compositions

**Ba and Li Insertion**



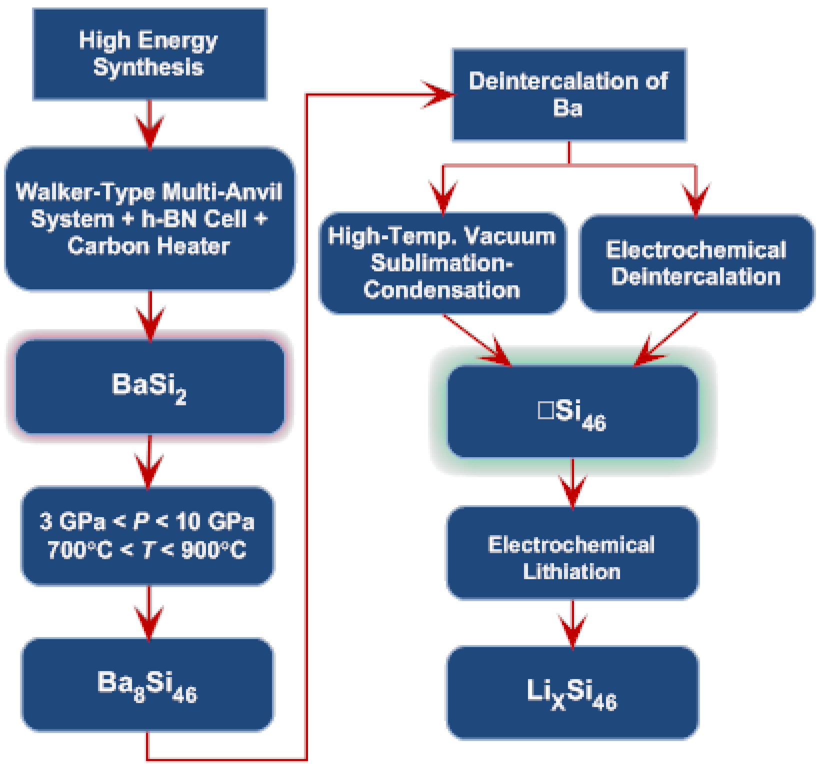

**Stabilization Energy vs. T**

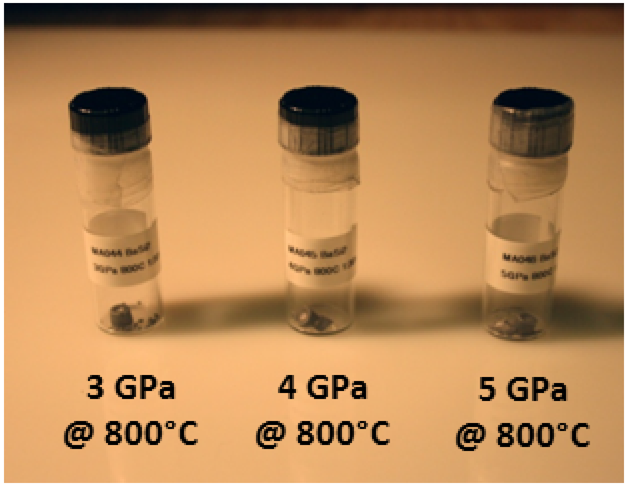


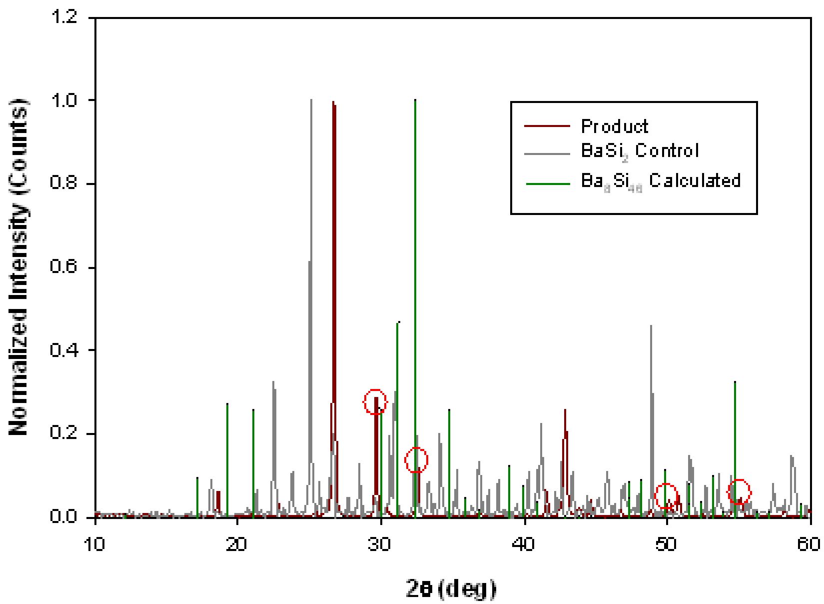

Li atoms are easier to extract from Al-substituted Si clathrates than Ba atoms

# *Accomplishments – Multi-Anvil Synthesis*

## *High-Energy Multi-Anvil Synthesis of $Ba_8Si_{46}$*



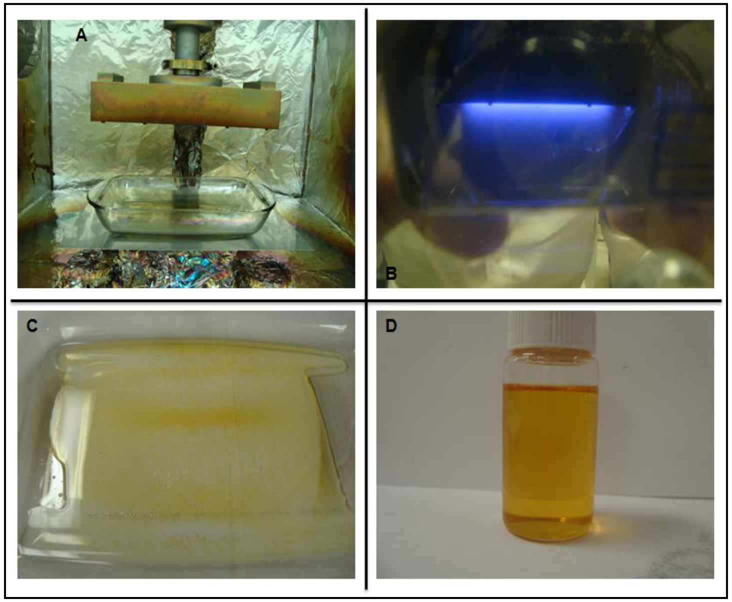



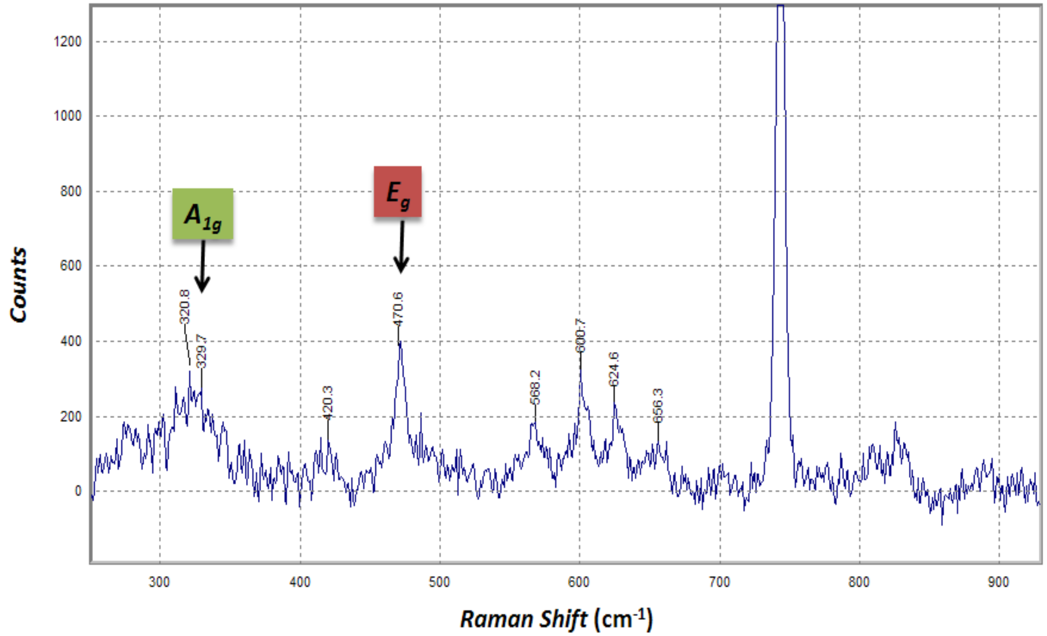




- PXRD indicates partial allotropic conversion of $BaSi_2$ to form $Ba_8Si_{46}$
- Structural impurity remains even after 5 GPa @ 800°C, due to stability of $BaSi_2$ (compared with the more reactive NaSi)
- Synthetic pathway not selected due to low yield and scalability

# Accomplishments - PEMS Synthesis

## *Direct Synthesis of Guest-Free Type I Silicon Clathrate – Plasma Magnetron/Imidazolium IL*



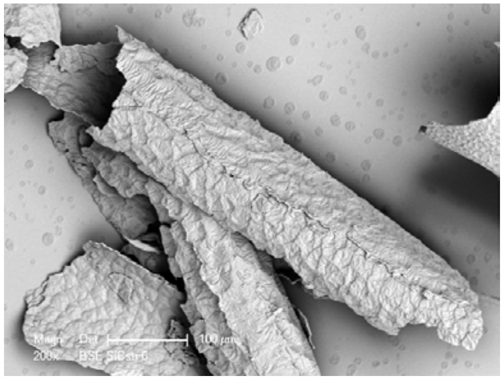



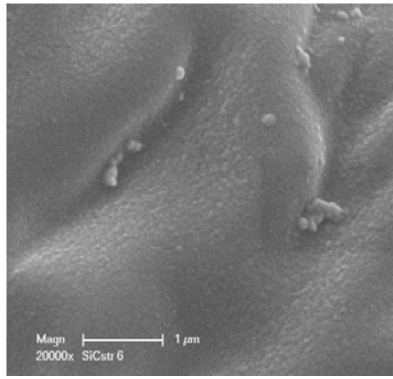

- Particle size and quantity too small to acquire PXRD
- NIR Raman spectroscopic microanalysis used to acquire the vibrational (phonon) spectrum
- First principles and normal mode computations were carried-out to predict Raman-active fundamental modes
- Synthetic pathway not selected due to low yield

Raman spectroscopic evidence for the formation of guest-free silicon clathrate (Type I) acquired from PEMS-synthesized nanoparticles. The positions of the theoretically-predicted $A_{1g}$ and $E_g$ phonon modes are shown.

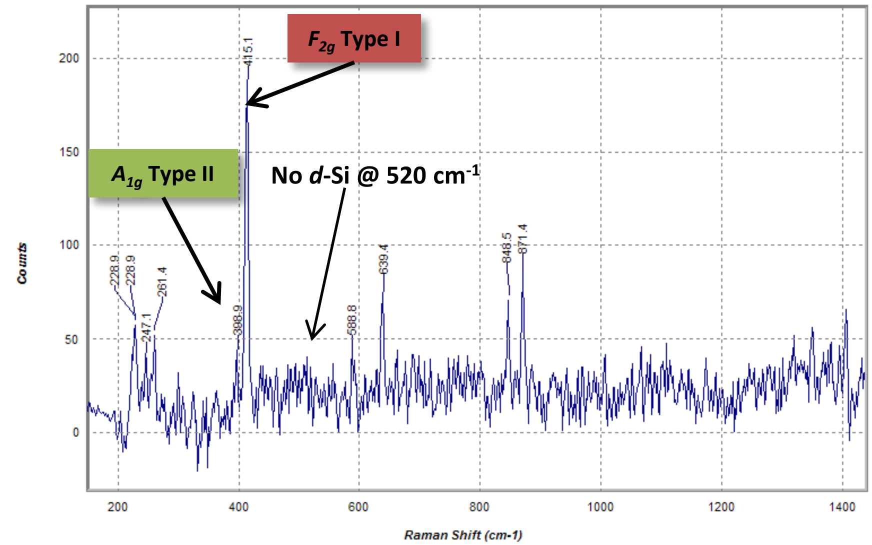
# Accomplishments - PEMS Synthesis

## *Direct Synthesis of Guest-Free Type I Silicon Clathrate – Plasma Magnetron/Castor Oil*

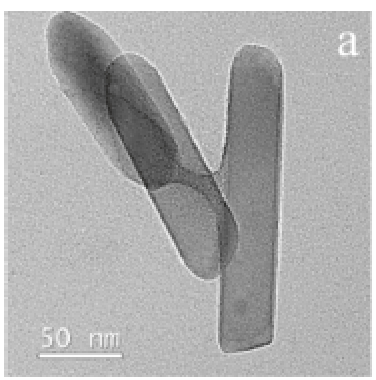


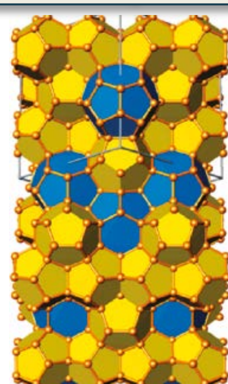



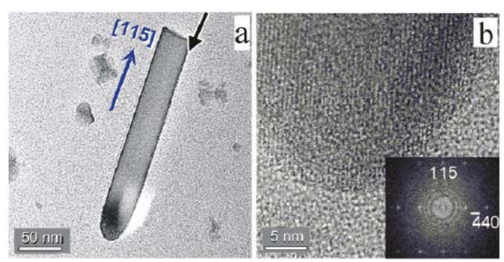

*SEM (backscattering) images of clathrate network particles formed from plasma-enhanced magnetron sputtering into pool of IL*




NIR Raman spectroscopic microanalysis shows large contribution of the $F_{2g}$ mode for Type I with a much smaller contribution from $A_{1g}$ mode, indicating that small domains of Type II clathrate were formed.






Simon, P. et al., *JACS*, 2011, *133*(19), 7596-7601

Rod-shaped, crystalline nanoparticles of $Na_xSi_{136}$ and $K_xGe_{136}$ (clathrate II) recently observed under HRTEM by Simon et al. 2011

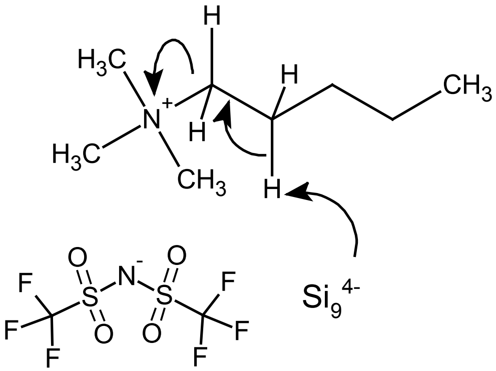
# Accomplishments - Solution Synthesis

## *Low Temperature Route to Synthesis of Guest-Free Type I Silicon Clathrate*

$$n[R'\text{-}CH_2\text{-}NR_3]^+ + X_y^{n-} \xrightarrow{\sim 300°C} yX^0\,[\text{Clathrate I}] + n[R'{=}CH_2] + nNR_3 + 2H_2$$

$R' = -(CH_2)_n-CH_3$
$R = -CH_3, H$
$X$ = Si, Ge, Sn
e.g., $BaSi_2 \Rightarrow Si_2^{2-}$
$Na_4Si_9 \Rightarrow Si_9^{4-}$

Slow oxidation of cluster anions ($X_y^{n-}$) and Hofmann-type elimination of an organic ammonium salt (ionic liquid)



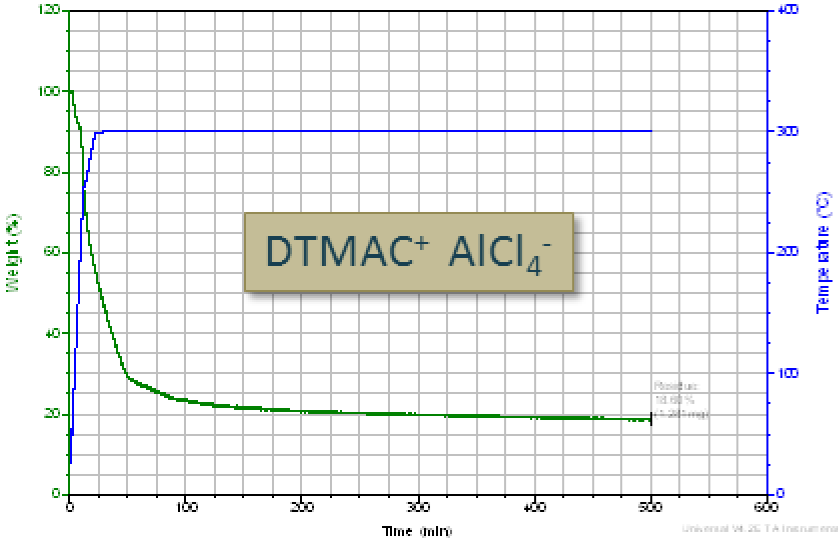

**First Step: Find or synthesize IL that is stable at high temperatures over at least 24 h:**

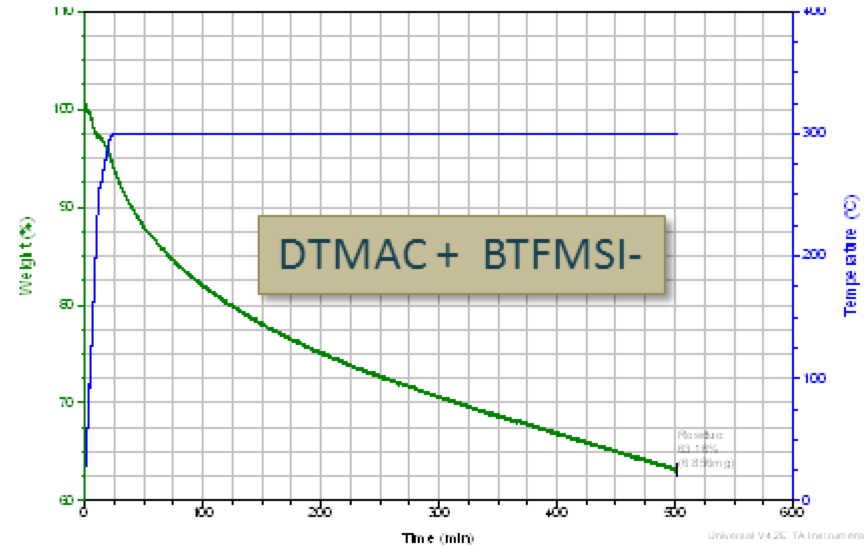
I. **Dodecyltrimethylammonium chloride (DTMAC)+ $AlCl_3$, forms liquid eutectic with $AlCl_4^-$.**
II. **Proprietary IL (sulfonyl imide anion), claimed to have high stability.**
III. **Synthesize bis(trifluoromethylsulfonyl)imide [BTFMSI] anion of DTMAC, should have high thermal stability.**

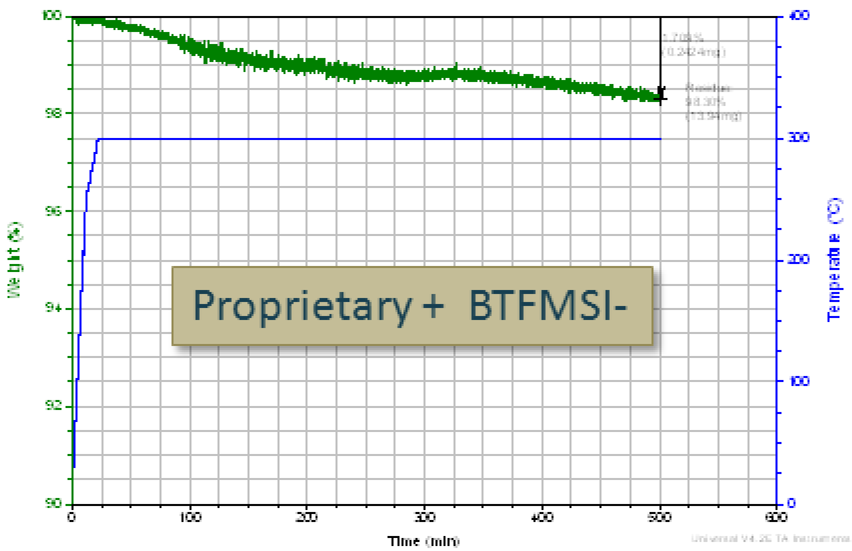
Grovenstein, E. Jr.; Stevenson, R.W. Carbanions III. Cleavage of tetraalkylammonium halides by sodium in liquid ammonia. *J. Am. Chem. Soc.* 1959, *81*, 4850-4857.
Guloy, A.M. et al. *Nature*, 2006, *443*, 320-323.

# *Accomplishments - Solution Synthesis*

## *Surveying the Thermal Stability of ILs*



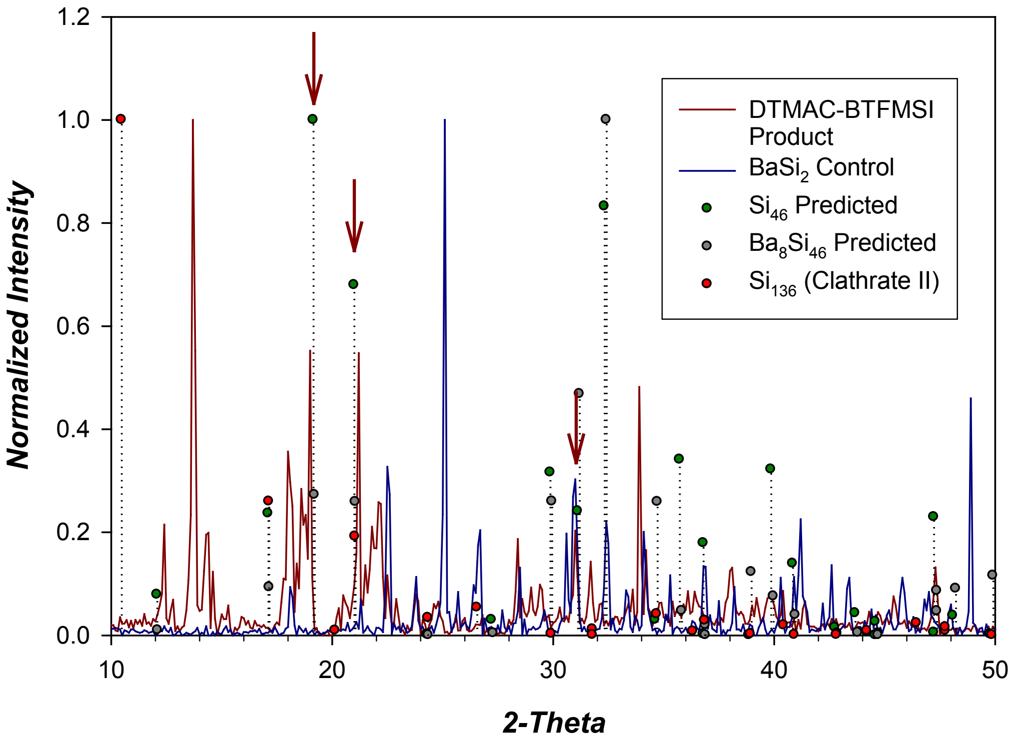




- DTMAC-BTFMSI ionic liquid also forms eutectic (like DTMAC-$AlCl_4$), transitioning to a liquid slightly above room temperature
- TGA shows that thermal stability is significantly improved with $BTFMSI^-$ counter ion
- Proprietary IL showed best thermal stability, but yielded no clathrate structure from silicide (attributed to unsuitable cation for reaction mechanism)

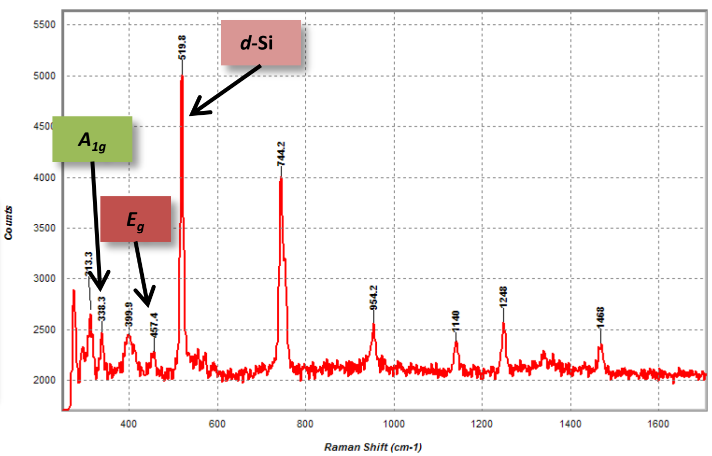
# Accomplishments - Solution Synthesis

## *Characterization of Products*



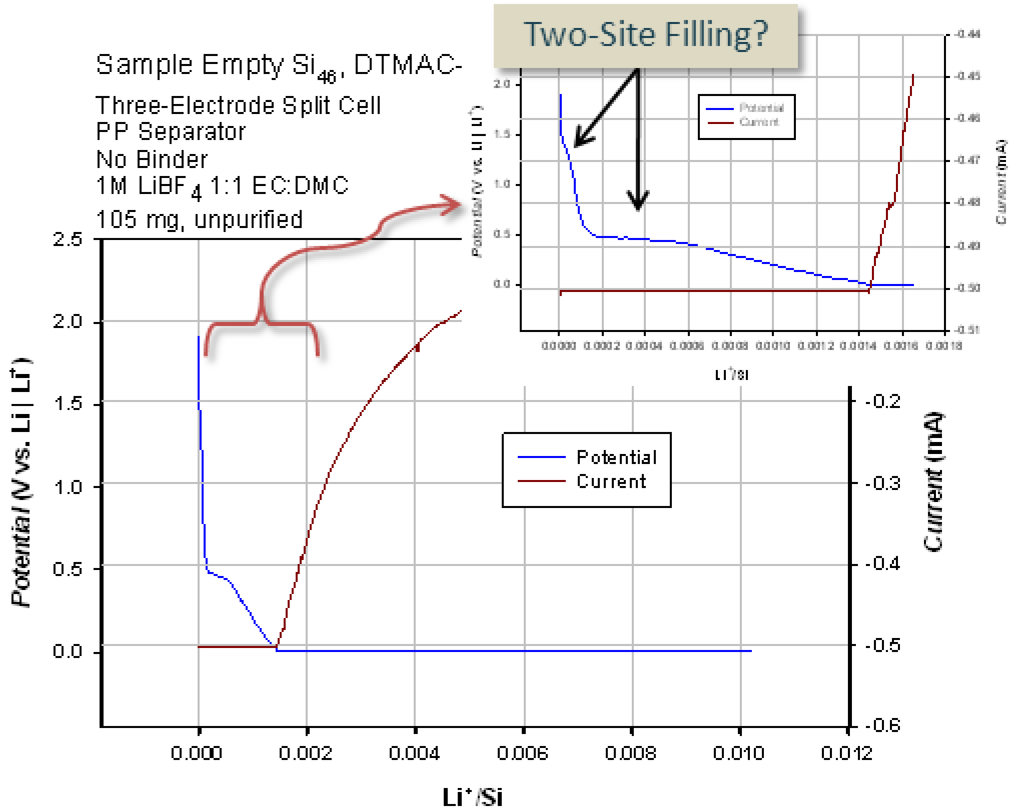

- PXRD shows evidence of structural transformation
- Several reflections of product are correlated with theoretical reflections of $Si_{46}$
- Type II clathrate $Si_{136}$ not formed as secondary or minor phase
- Purification method needed to remove unreacted $BaSi_2$, dodec-1-ene, and trimethylammonium chloride
- Product yield should improve with the more reactive NaSi

NIR-Raman spectrum shows evidence for the formation of guest-free silicon clathrate (Type I) as noted, along with unreacted silicide (*d*-Si) and organic side products. Reaction under these conditions does not yield the Type II clathrate ($Si_{136}$).

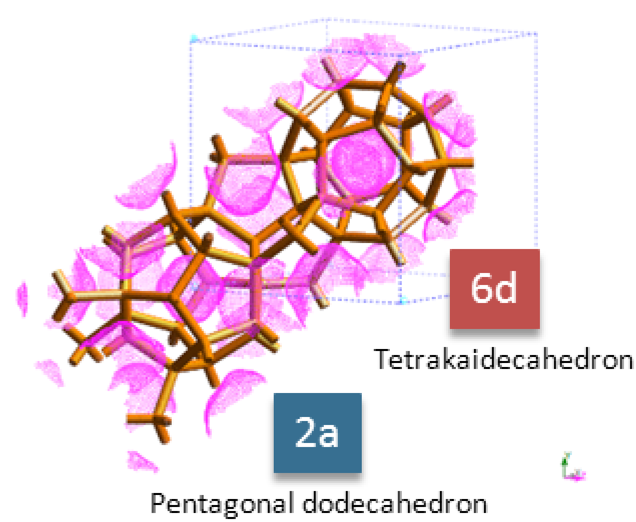


# Accomplishments - Solution Synthesis

## *Electrochemical Half-Cell Measurements*




- $Li^+$ cathodic intercalation into as synthesized $Si_{46}$ after SEI formation
- OCP: 2.59 V vs. Li | $Li^+$
- Two intercalation plateaus observed, possibly attributed to space-filling of the two framework polyhedra (2a and 6d sites) in $Si_{46}$
- $Li^+$ intercalation at C/100 rate is demonstrated, but may be constrained by initially-wide band-gap of empty $Si_{46}$ (2.5 eV)
- Assumes 100% purity, actual purity may be much lower (20-50%)



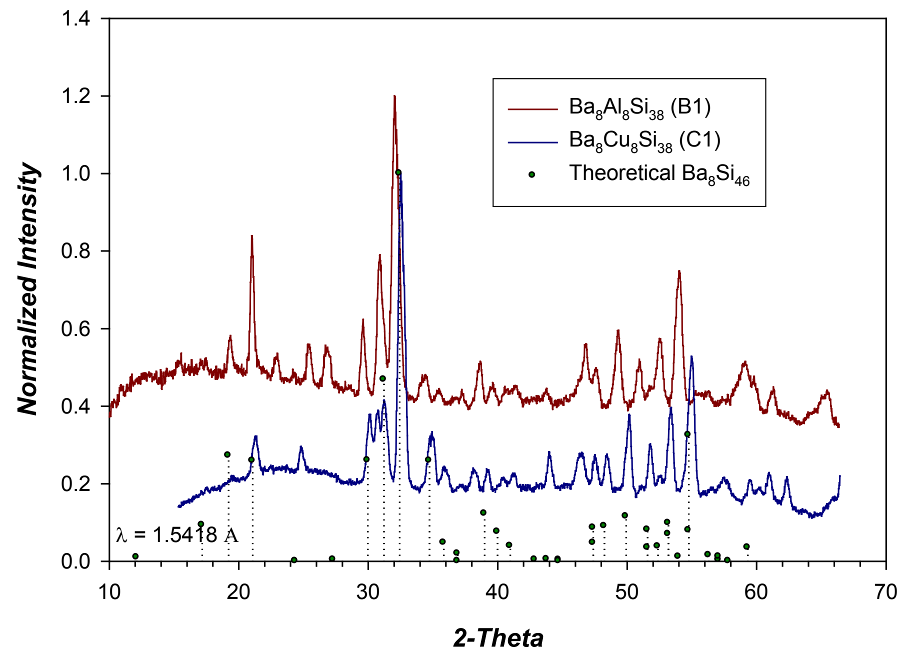

Electrochemical measurements show that $Li^+$ can be intercalated into as-synthesized empty Type I silicon clathrate ($Si_{46}$). Achieving theoretical capacities should be realized with understanding of, and improvements in, the formation of a stable SEI and appropriate electrode composition.

# *Accomplishments - Vacuum Arc-Melt Synthesis*

## *Synthesis of $Ba^{2+}$ Intercalated, Metal-Substituted Type I Silicon Clathrate via Arc Melting*

| | |
|---|---|
| A1 | $Al_8Si_{38}$ |
| A2 | $Al_xSi_{38}$ |
| B1 | $Ba_{7.85}Al_8Si_{38}$ |
| B2 | $Ba_{7.95}Al_8Si_{38}$ |
| C1 | $Ba_{8.1}Cu_{8.5}Si_{38}$ |
| C2 | $Ba_{7.9}Cu_{7.9}Si_{38}$ |

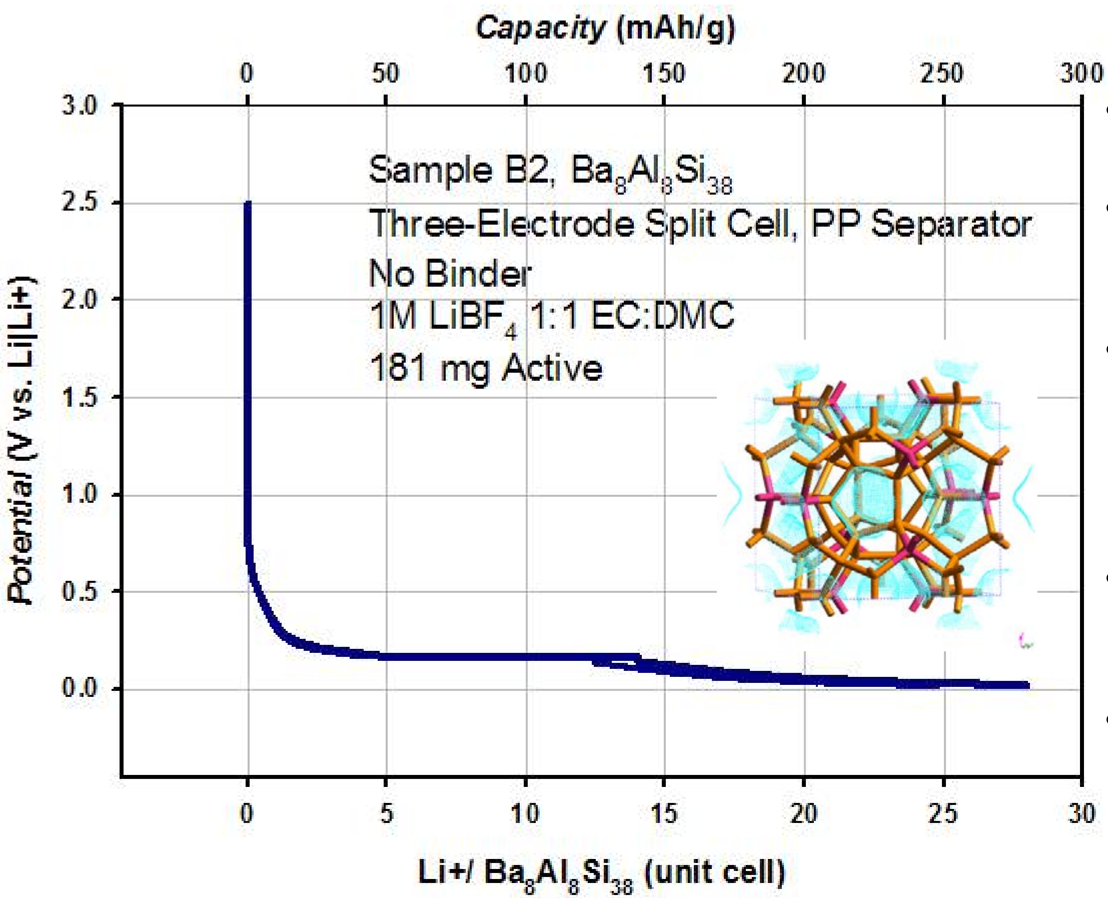
- Al- and Cu-substituted Type I silicon clathrates successfully formed, though only possible in the presence of guest atoms (Ba)
- Arc-melting process yielded material of high structural purity without secondary phase formation of Type II clathrates or *d*-Si
- Other compositions consisting of different framework substitutions and guest atoms are also possible




*Materials prepared for SwRI by Candace Chan, ASU*

# Accomplishments - Vacuum Arc-Melt Synthesis

## *Electrochemical Half-Cell Measurements: Capacity Analysis without Binder*

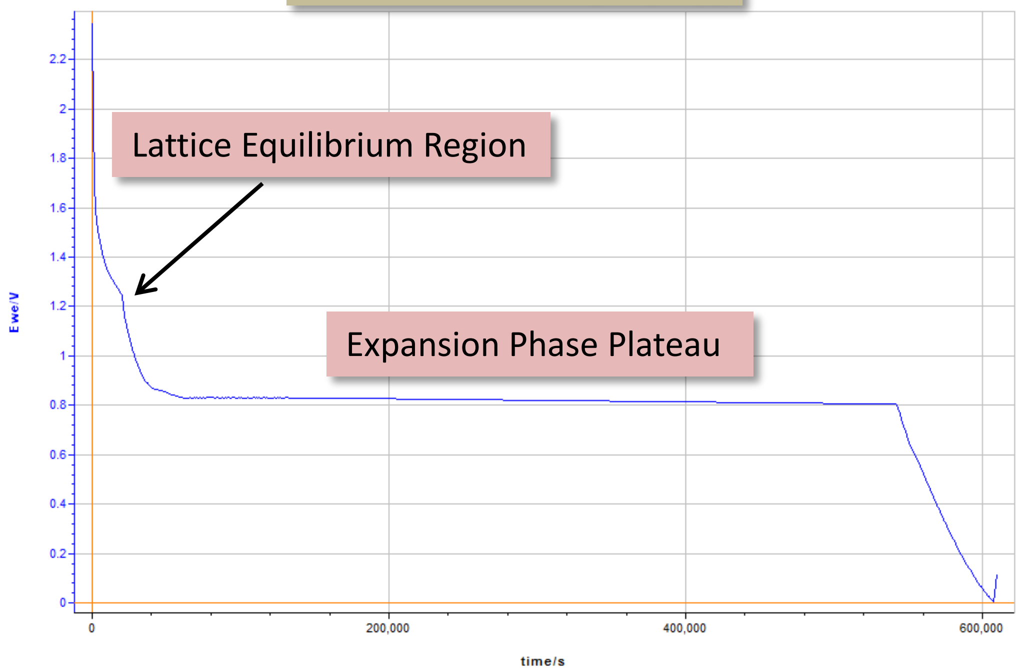


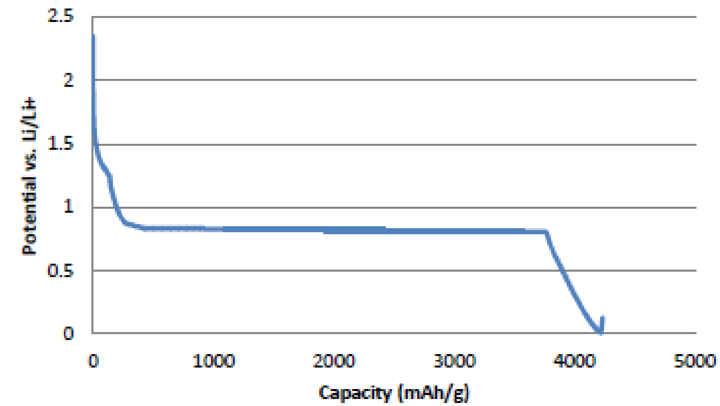

- Cathodic intercalation of $Li^+$ into $Ba_8Al_8Si_{38}$ clathrate electrode
- Pressed electrode, mechanically stable without binder or conductive additive
- First cycle capacity is shown within the lattice equilibrium range (i.e., up to the theoretically-predicted number of Li atoms without lattice expansion)
- Li ions intercalate into lattice guest sites even while Ba guest atoms are tightly bound
- Higher capacities are achievable with lattice expansion $\Rightarrow$ next slide

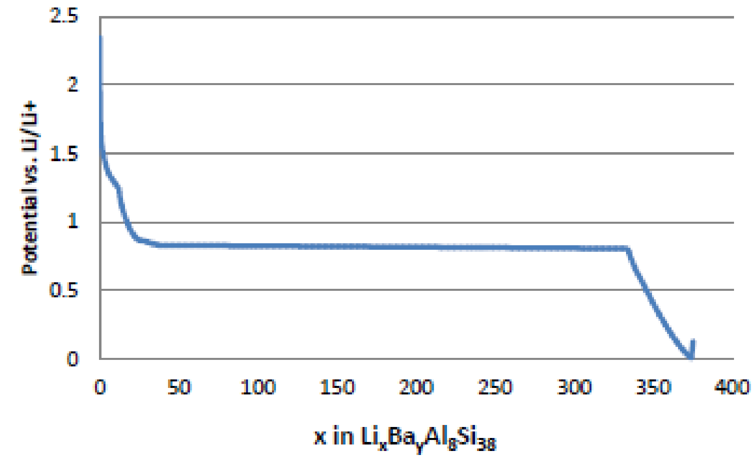
# *Accomplishments - Vacuum Arc-Melt Synthesis*

## *Electrochemical Half-Cell Measurements: Beyond the Lattice Equilibrium Region*

Sample B1 $Ba_8Al_8Si_{38}$



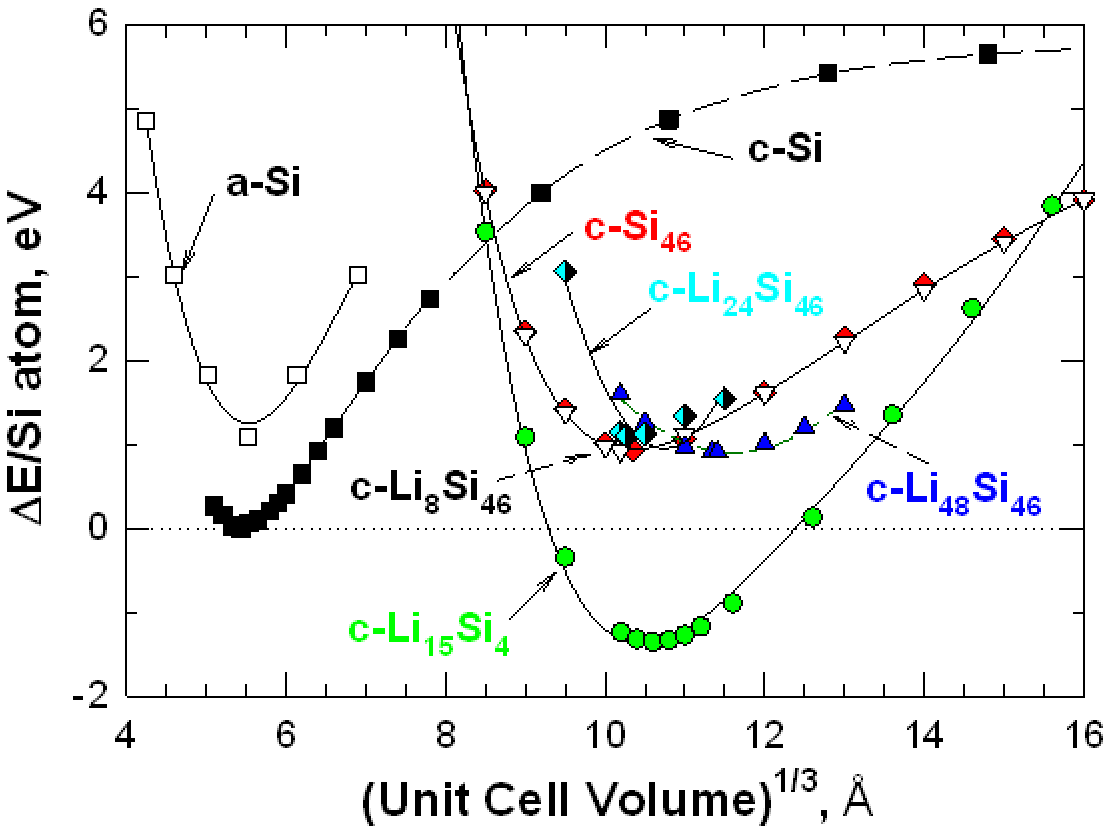

- Lattice equilibrium region; i.e., little or no lattice expansion for x < 50
- Expansion phase plateau may be accompanied by lattice expansion ⇒ first-principles calculations underway to assess degree to which lattice expands in this phase

300 – 350 $Li^+$ intercalated into Ba-occupied lattice: corresponds to 8-9 Li+/Si

*Measurements made by Candace Chan, ASU, for SwRI*

# Accomplishments - Computations

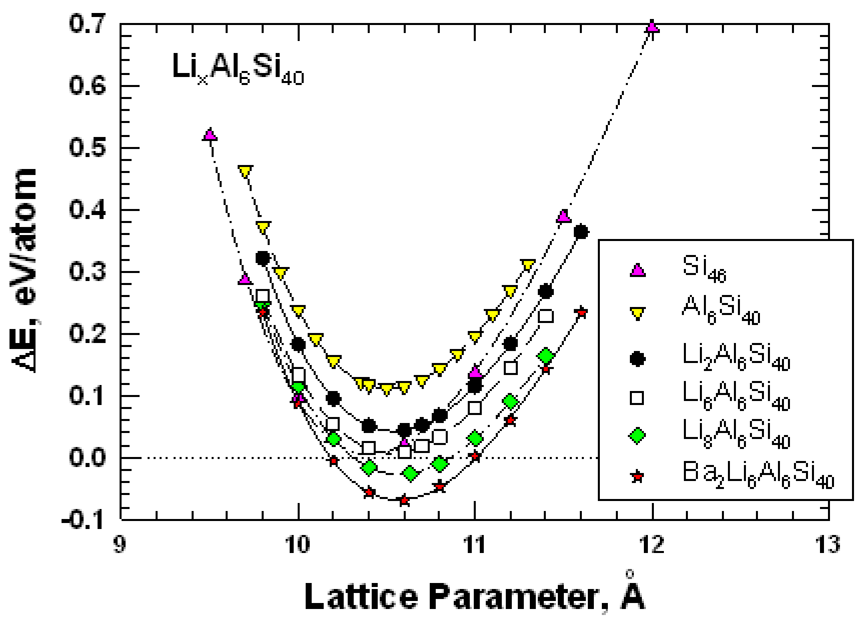
## Computed Energies of Formation for Li Insertion in $Si_{46}$

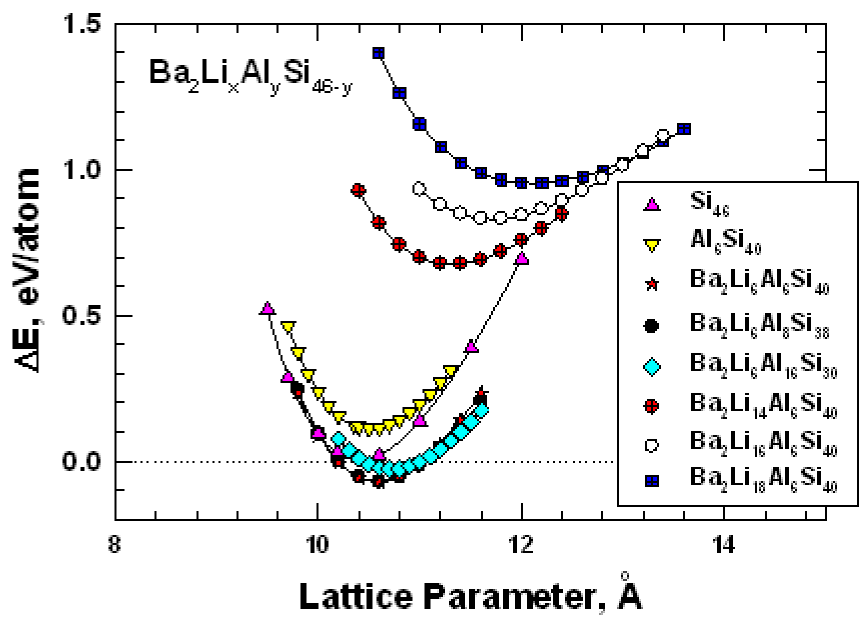



- Up to 48 Li atoms can be inserted into empty $Si_{46}$ without causing significant lattice expansion
- The unit cells of $Li_xSi_{46}$ and $Li_{15}Si_4$ are comparable in volume

# *Accomplishments - Computations*

## Computed Energies of Formation for Ba and Li Insertion in Various Type I Clathrate Compositions



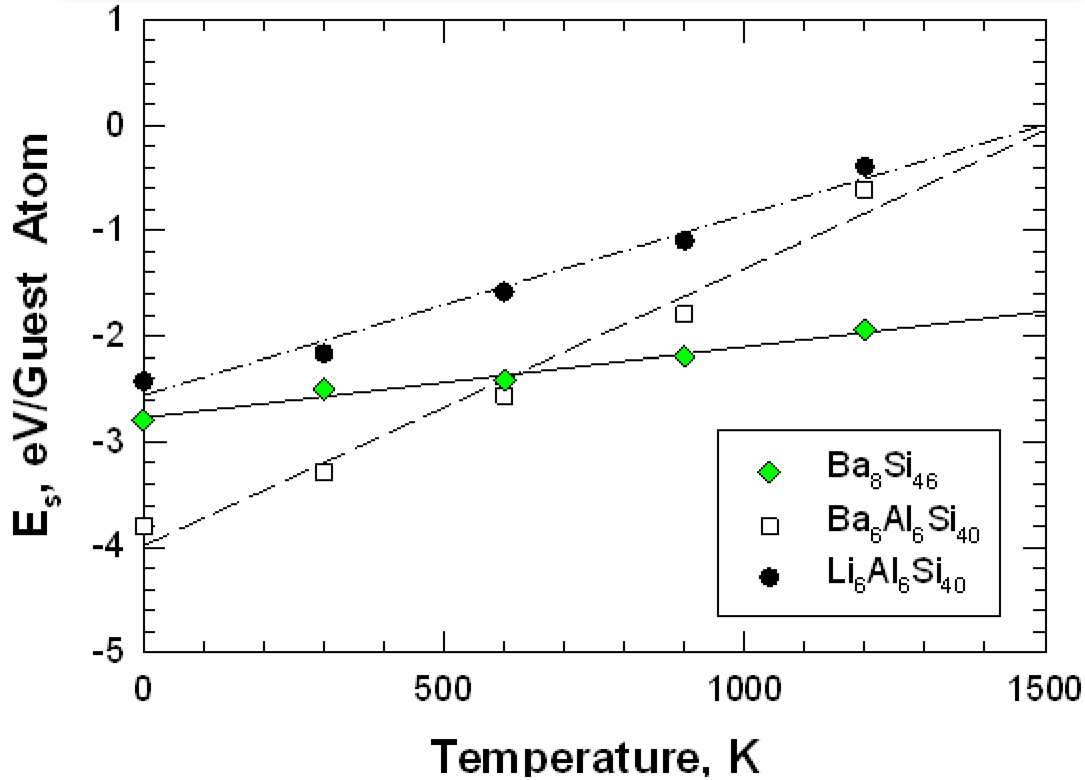




Al-substituted Si clathrates with Ba holds fewer number (less than 48) Li guest atoms than empty Si46 clathrates when the unit cell begins to expand.

# *Accomplishments - Computations*

- Ba and Al stabilize the clathrate structure better than Li, making Ba guest atoms difficult to remove at any temperature
- Li atoms are relatively easy to remove from the clathrate structure
- Theoretical results are consistent with experimental observations: small anodic current for deintercalation of Ba

## Stabilization Energy vs. Temperature



# *Collaborations*

- Dr. Candace K. Chan, Assistant Professor, Materials Science & Engineering, Arizona State University, Tempe, AZ: Providing materials, process expertise, and initial EC data on arc-melt synthesis of metal-substituted silicon clathrates; co-inventor
- Dr. Jiuhua Chen, Assoc. Professor, Assoc. Director of the *Center for the Study of Matter at Extreme Conditions* (CeSMEC), Mechanical and Materials Engineering Department, Florida International University, Miami, FL: Provided laboratory services and technical expertise on multi-anvil synthesis

# *Future Work*

- Perform first-principles (DFT and CPMD) computations to identify possible reaction pathways for the formation of empty clathrates $Si_{46}$, $Li_xSi_{46}$, $Li_{15}Si_4$, and $Li_xM_ySi_{46-y}$.
- Synthesize hundreds of grams of Type I silicon clathrates and/or metal-silicon Type I clathrate alloys with complementary determination of structural purity via down-selected processing methods (arc-melting and solution synthesis method).
- Continue half-cell electrochemical characterization tests on silicon clathrate anodes prepared from empty $Si_{46}$ and metal-substituted Type I silicon clathrate ($M_8Al_8Si_{38}$) materials

# *Summary*

- Selected two pathways for synthesis of Type I silicon clathrate compounds:
  - Bulk solution, Hofmann-type oxidation-elimination reaction in IL at elevated temp.
  - Vacuum arc melting (for metal-substituted clathrate alloys)
- Demonstrated the structural transformation of silicide to clathrate compositions, though yield needs further improvement in the case of solution synthesis
- $Li^+$ intercalation into pure (empty) and metal-substituted (alloy) silicon clathrates has been experimentally validated, consistent with theoretical predictions
- First principles DFT and CPMD computations predict excess stability (exothermic) of Ba guest atoms in clathrate structures, compared with Li guests, which explains why Ba guest atoms are difficult to remove by electrochemical means

# *Project Team*

Carol A. Ellis-Terrell, M.S., Research Scientist: *material synthesis, EC measurements*

Wuwei Liang, Ph.D., Sr. Research Engineer: *DFT and CPMD computations*

Thomas L. Booker, Engineering Technologist: *engineering design and measurements*