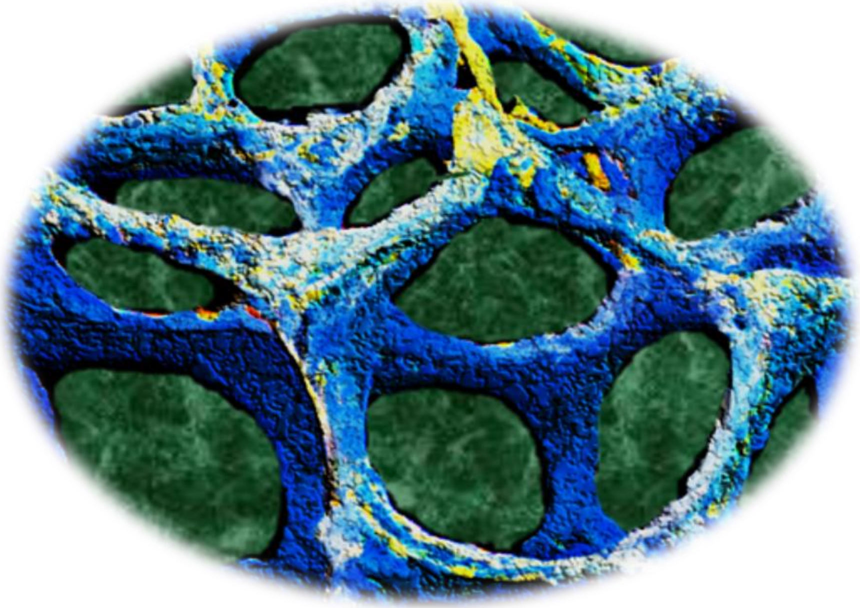
High-Density, Low-Hysteresis Storage Using Hydrated Salts in Surface-Functionalized Hydrogels



Performing Organization(s): University of Illinois, AO Smith
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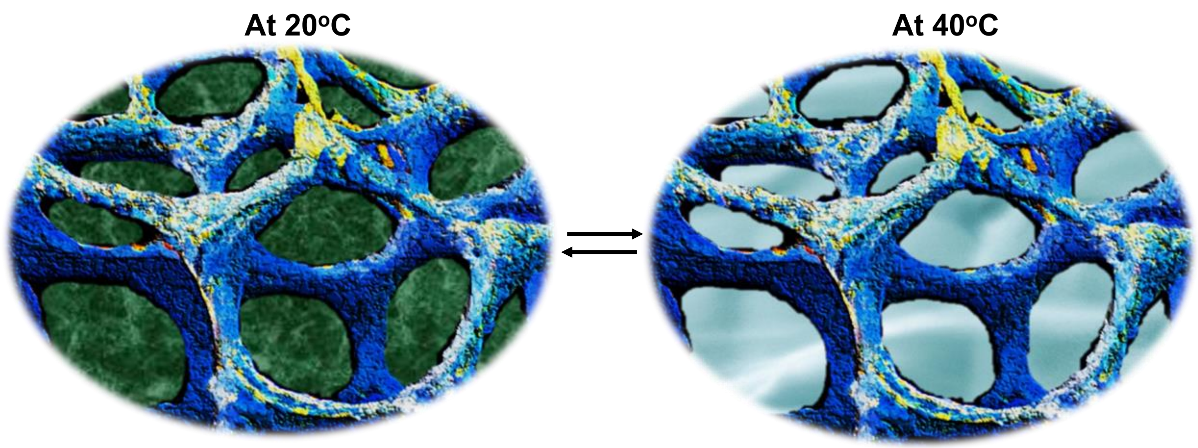
WBS #, FOA Project # and/or any other Project # DE-EE0009680

Project Summary

Objective and outcome

Develop and validate a ***thermal storage material*** based on Glauber's salt (GS)

- at a composite material cost of ≤$2.5/kWh at 1 ton scale
- storage density ≥80 kWh/m^3
- thermal conductivity of the composite ≥0.75 W/mK
- retained energy density of ≥75% over ≥100 thermal cycles



(Solid) Sodium sulfate decahydrate

(liquid) Ions, glycine water, Sodium sulfates

Team and Partners

Lead: University of Illinois at Urbana-Champaign

Partner: AO Smith

Stats

Performance Period: 10/1/21 to 9/30/23

DOE budget: $1.512 M, Cost Share: $381 k

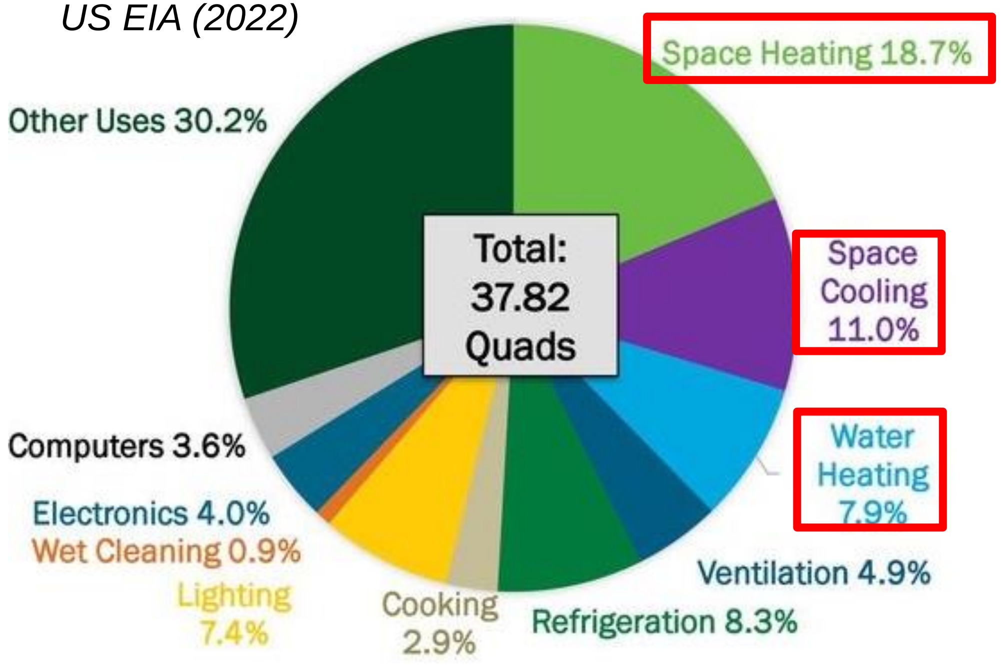
Milestone 1: Demonstrate suitable chemistry

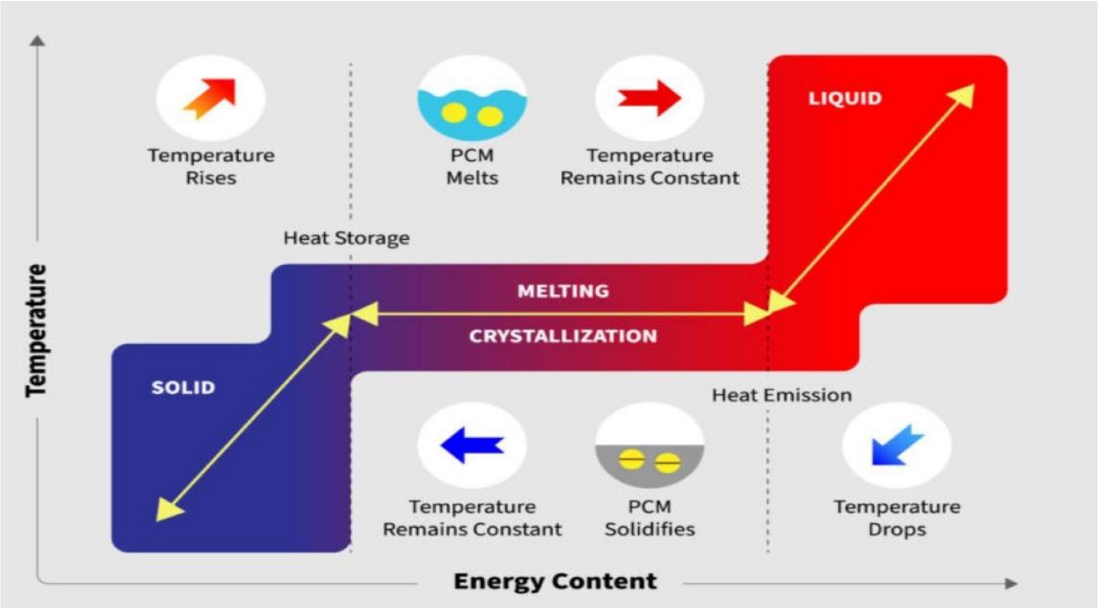
Milestone 2: Demonstrate performance over >100 cycles

Problem

Building Energy Use

US EIA (2022)





Thermal storage based on PCM can increase efficiency and accelerate electrification

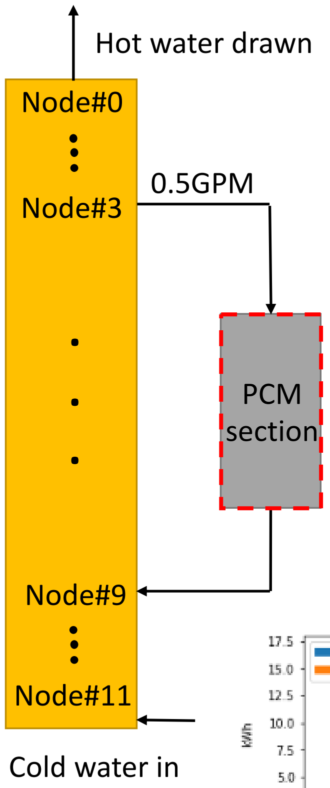
- \+ High storage density (~2x paraffin)
- \+ Low cost (~$100/ton)
- \+ Melting point of 32.4°C

Sodium sulfate decahydrate (**SSD**)

Why can't we do this today?

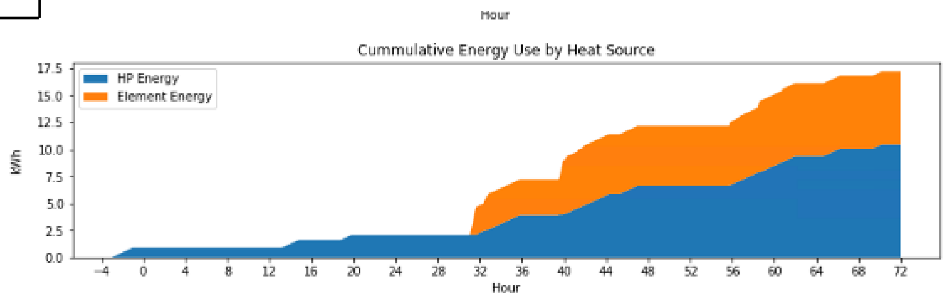
Supercooling – don't get back what you put in
Phase Segregation – doesn't last

Alignment and Impact

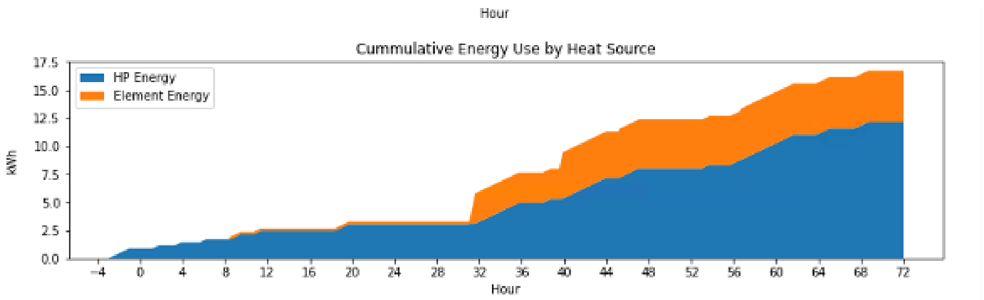


Development of GS-based PCM that meets project metrics can enable thermal storage solutions in building HVAC and water heating

- Cost ≤$2.5/kWh at 1 ton scale
- Storage density ≥80 kWh/m^3, thermal conductivity ≥0.75 W/mK
- Exergetic efficiency – supercooling < 2C
- Stability - Retained energy density of ≥75% over 100s cycles



- HP Energy Use: 10.455kWh/9.57kWh
- Element Energy Use: 6.75kWh
- Total Energy Use: 17.205kWh/16.32kWh
- 3 Day COP: 2.519
- Minutes demand unsatisfied: 21

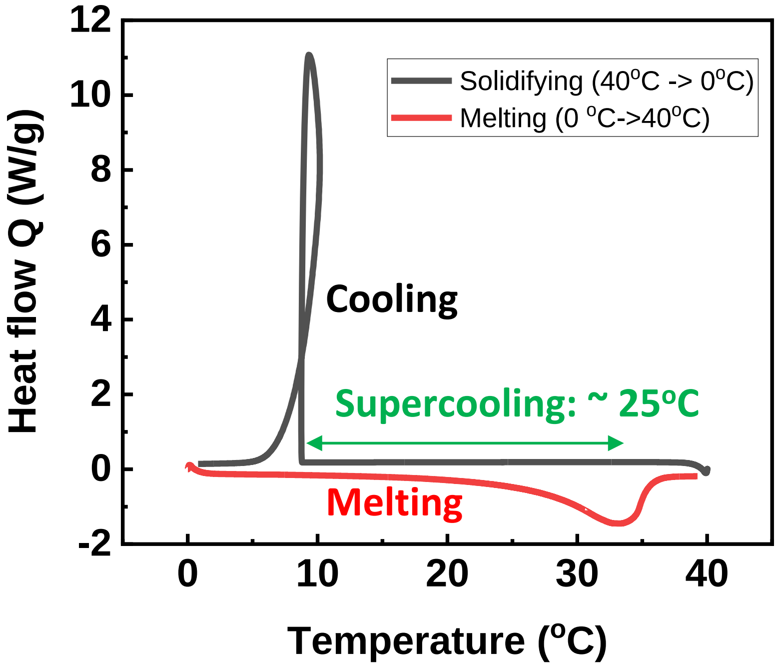


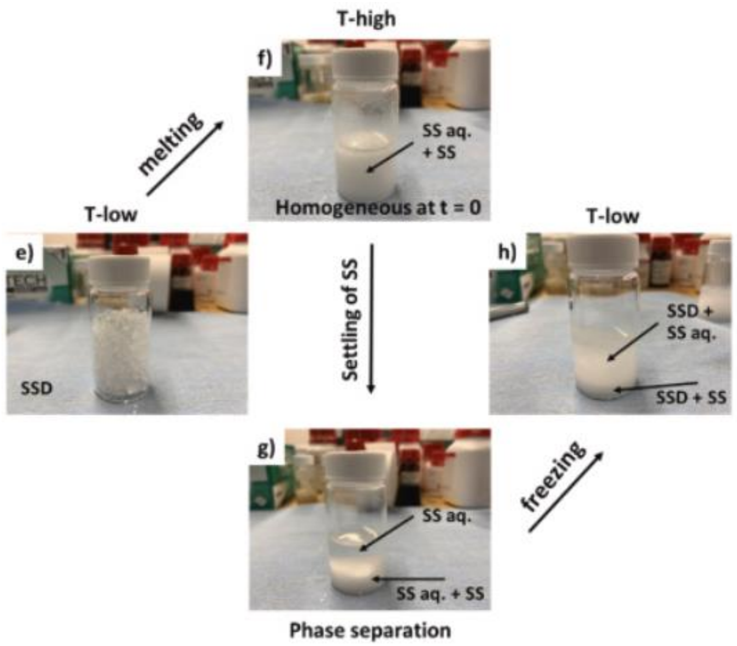
- HP Energy Use: 12.165kWh/10.478kWh
- Element Energy Use: 4.575kWh
- Total Energy Use: 16.74 kWh/15.05kWh (1.27kWh saved)
- 3 Day COP: 2.817 (0.298 increased)
- Minutes demand unsatisfied: 15 (28% reduced)

Glauber's Salt as a PCM

$$Na_2SO_4 \cdot 10H_2O\ (s) \overset{1}{\longleftrightarrow} 2Na^{+}(aq) + SO_4^{2-}(aq) + 10H_2O\ (l) + \Delta H$$

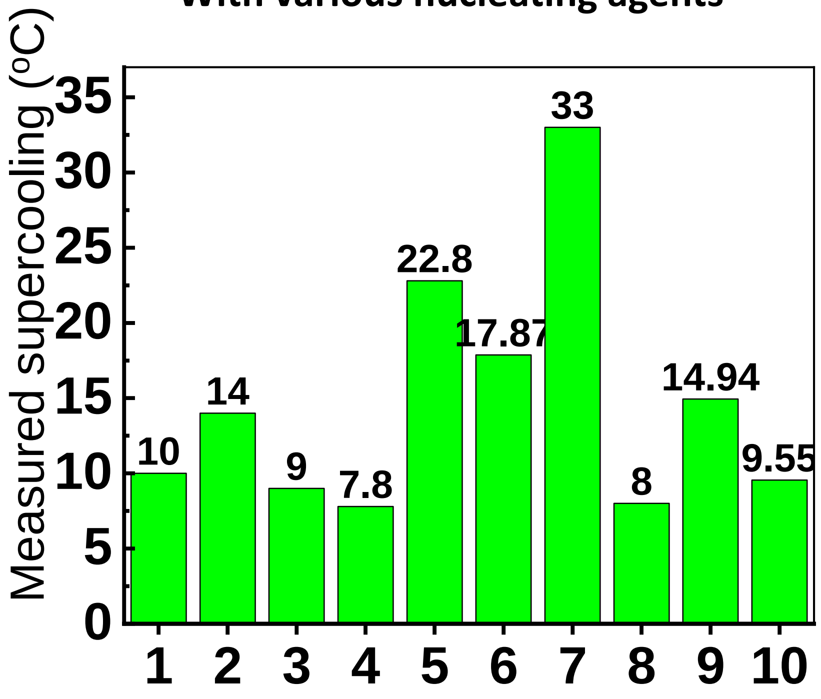
$$\overset{2}{\longrightarrow} Na_2SO_4\ (s) + 10H_2O\ (l)$$





Composites Part B (2022)

With various nucleating agents

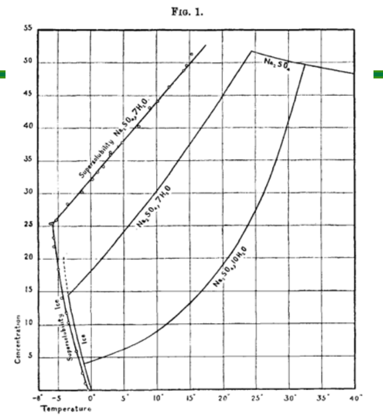


Brief History of GS in Thermal Storage

- 1658 – Discovery and medicinal use

courtesy: Wikipedia

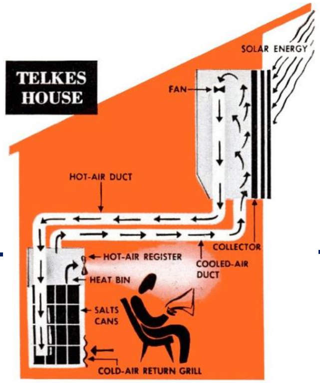
- 1890–1900s: Spontaneous crystallization and supersaturation studies

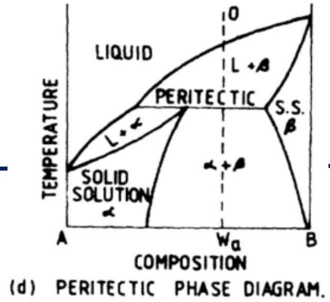


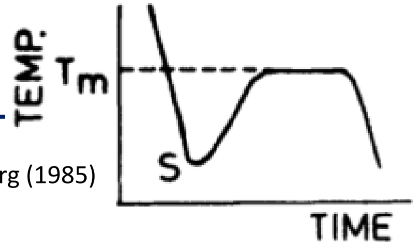
Hartley et al., 1908

- 1952 **Telkes** – supercooling and incongruent melting

courtesy: Britannica

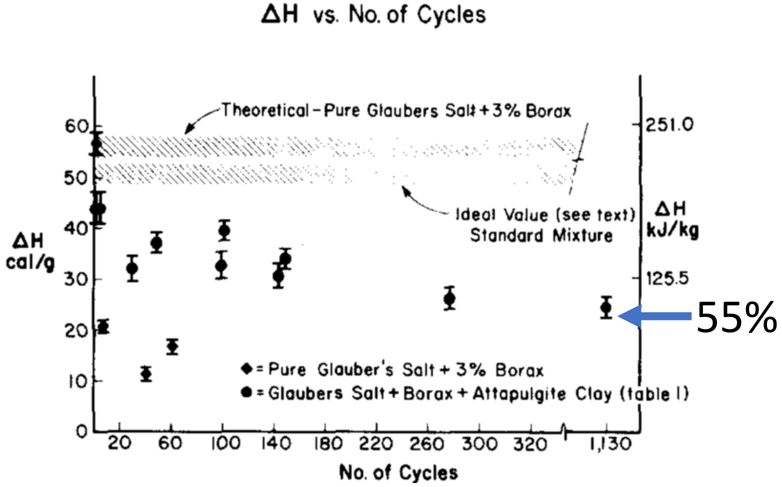




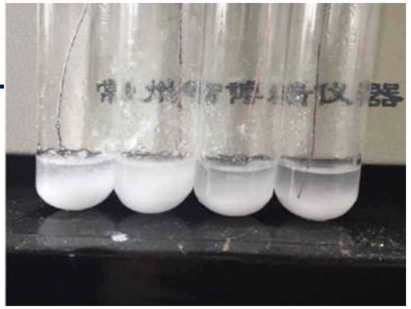


Garg (1985)

- 1970s - Solar energy storage
- 1980 **Marks** - mm-scale crystal growth causing inhomogeneity of solution, preventing cycling



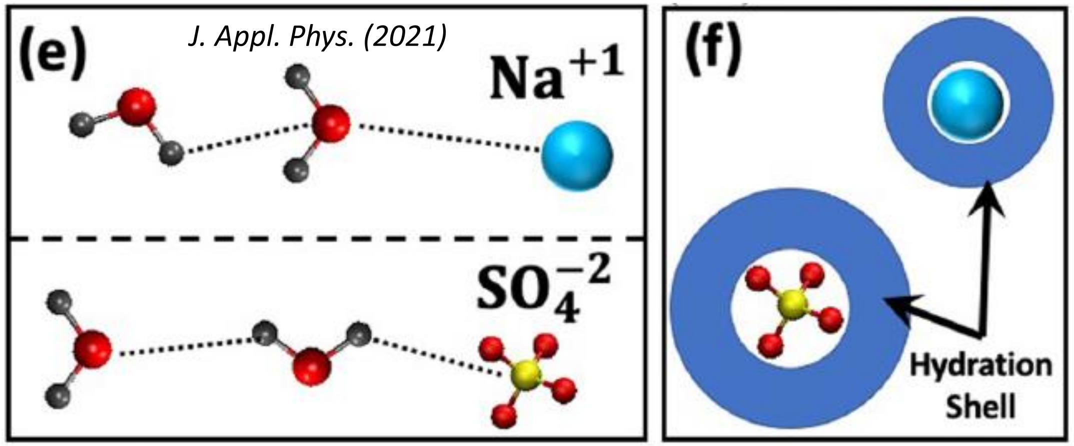
- 2000s - New thickeners and high thermal conductivity additives



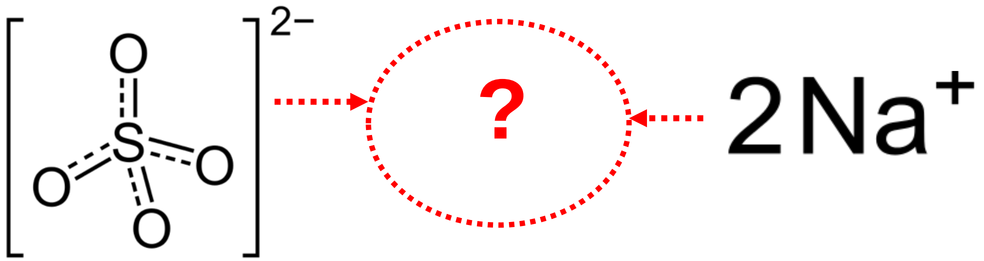
GS and borax - phase stratification with 3-6% PAA (Dong et al. 2020)

Key Idea

Problem 1: Supercooling

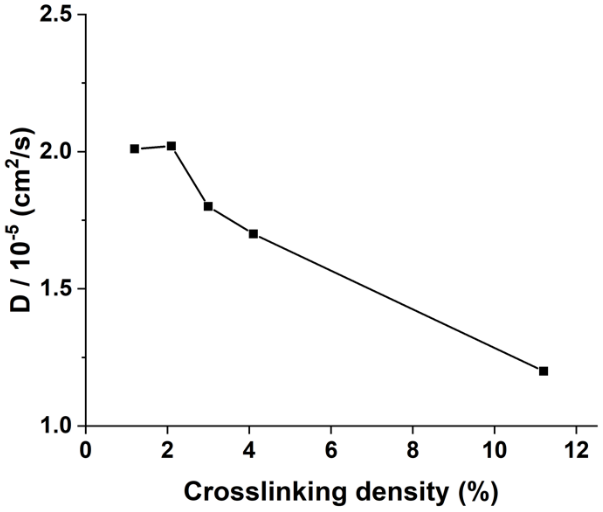


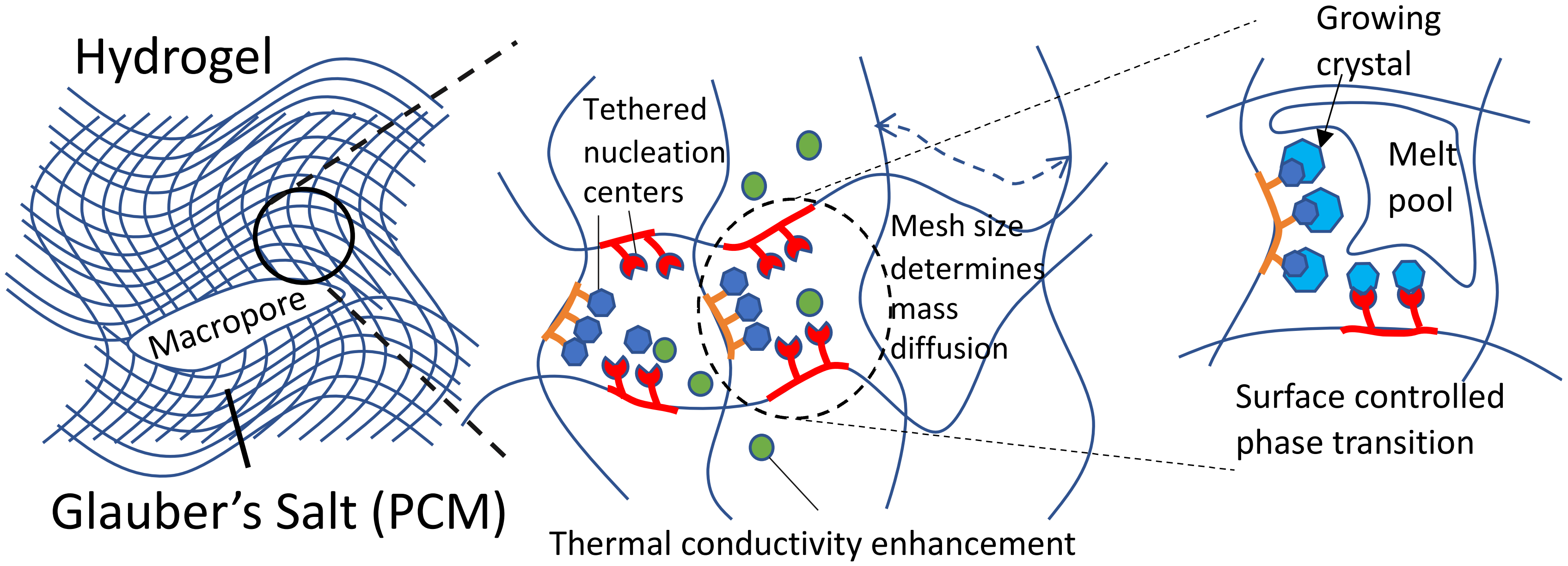
Solution – Look for nucleating agent that hinders hydration shell e.g.



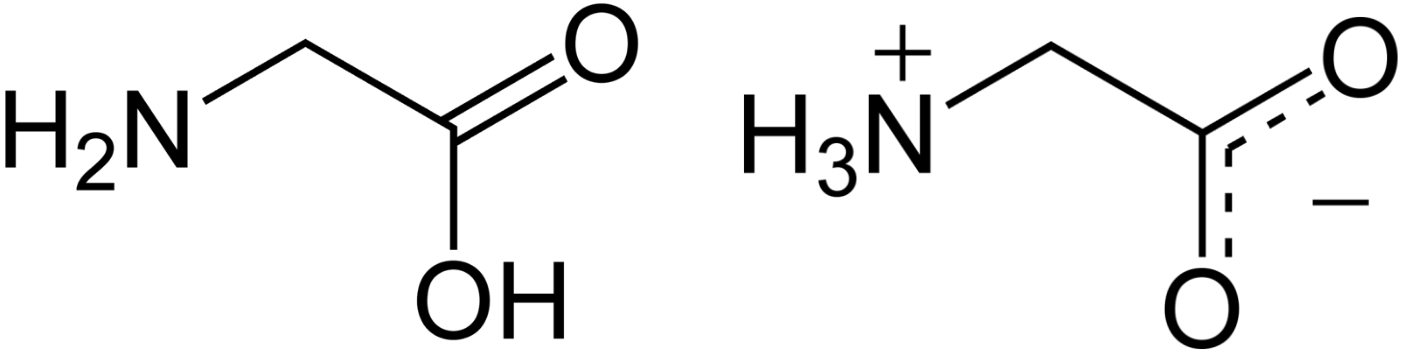
Strong electrostatic attraction causes hydration shell around ions, hindering SSD from nucleating

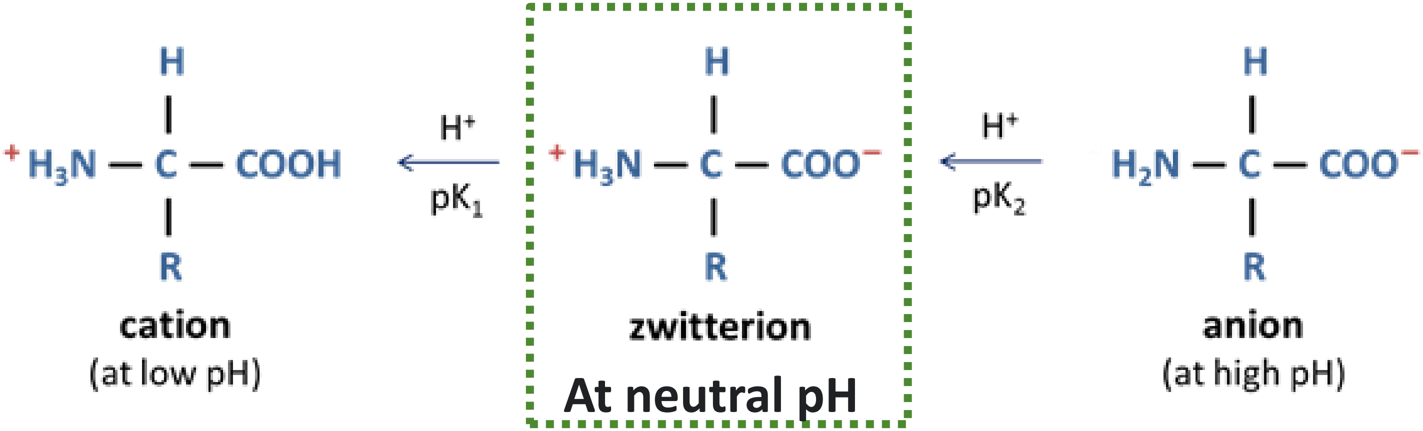
Problem 2: Phase segregation

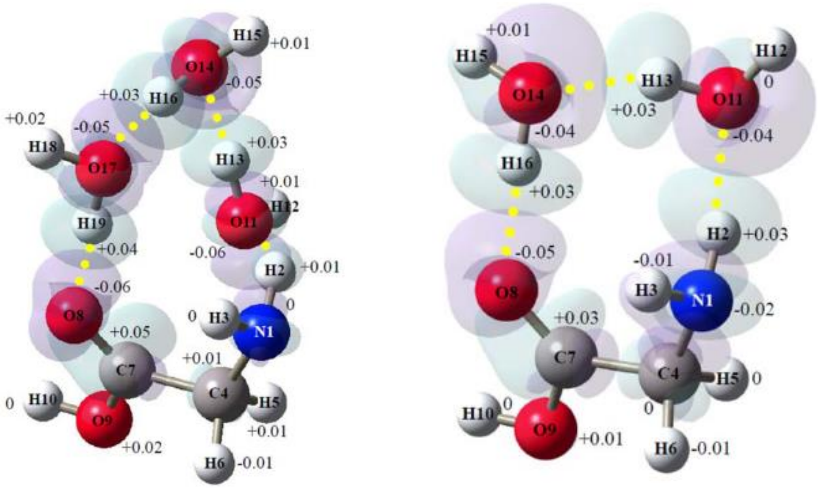




Glycine; Zwitterion form



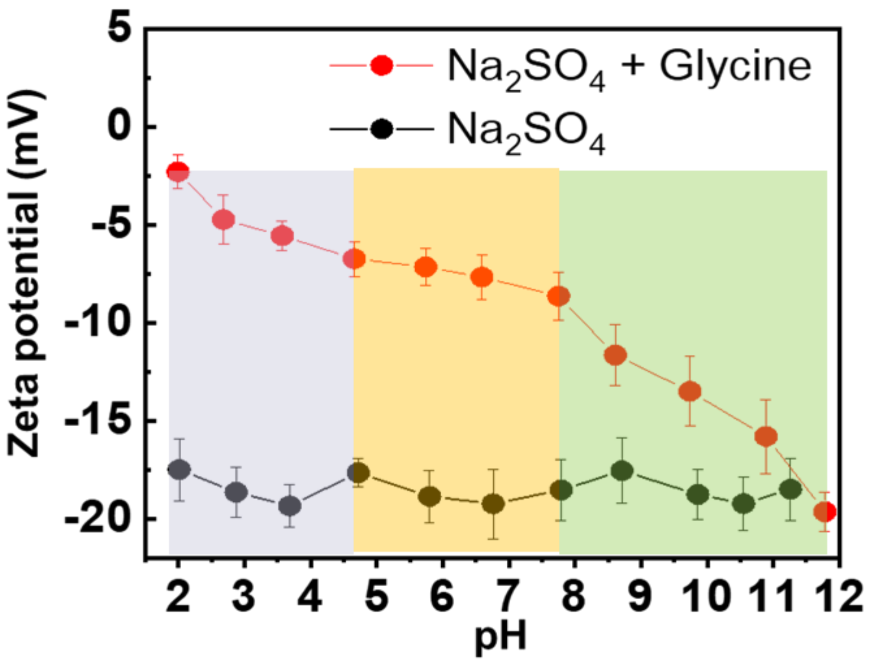


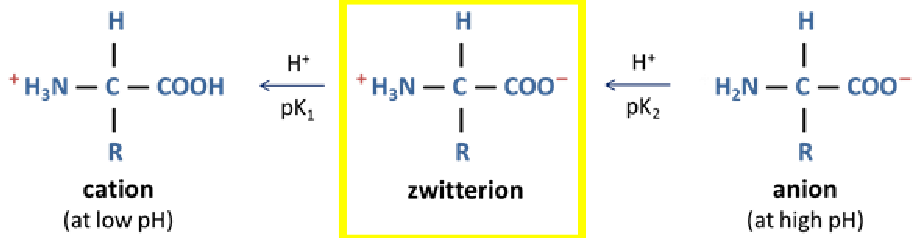


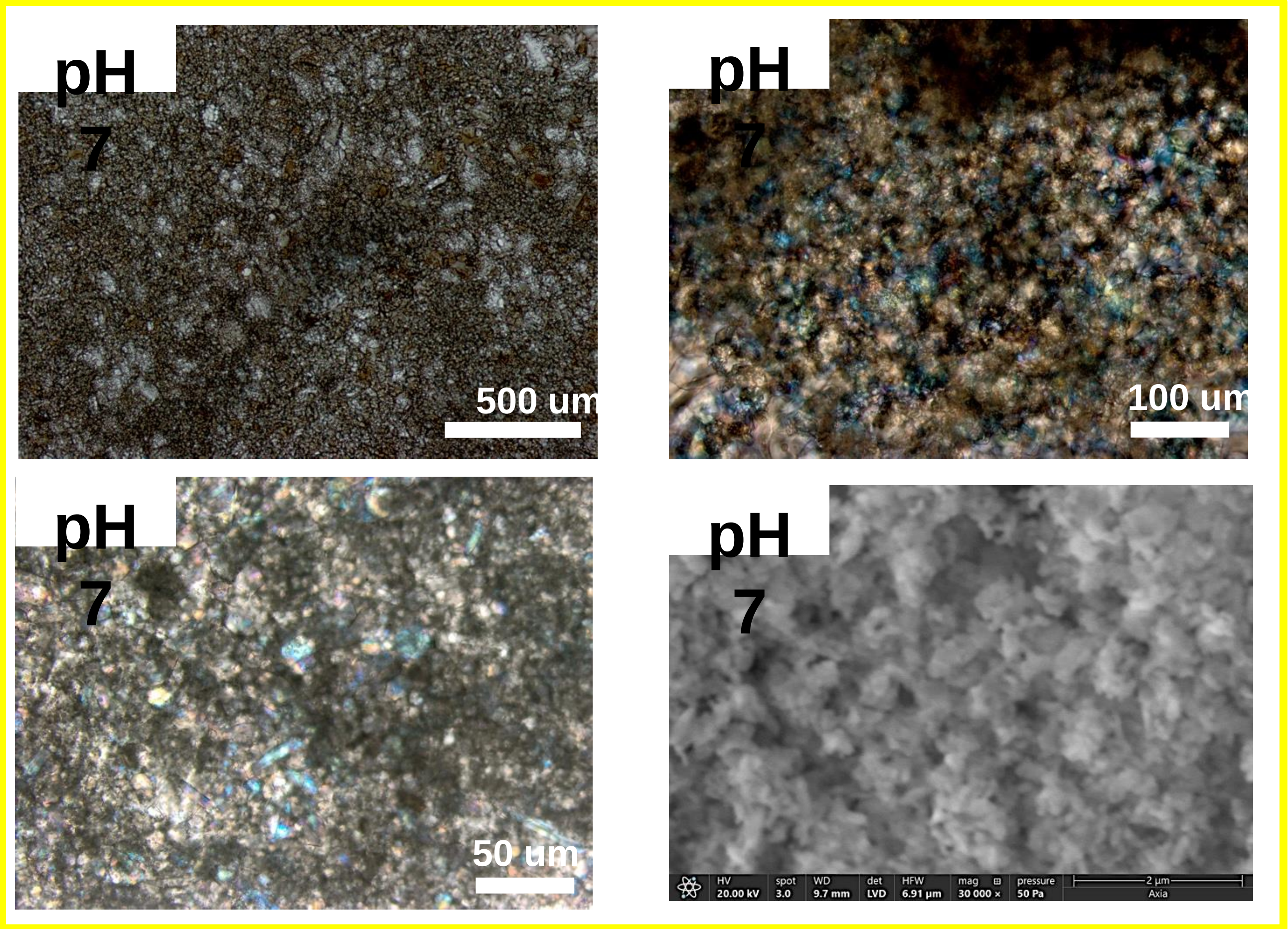
Int J Quantum Chem. 2018

- Multiple hydrogen-bonds can be formed with glycine.
- Glycine is Zwitterionic properties at neutral pH, which means it has both a positive and a negative charge

Glycine; Morphology-controlled crystal



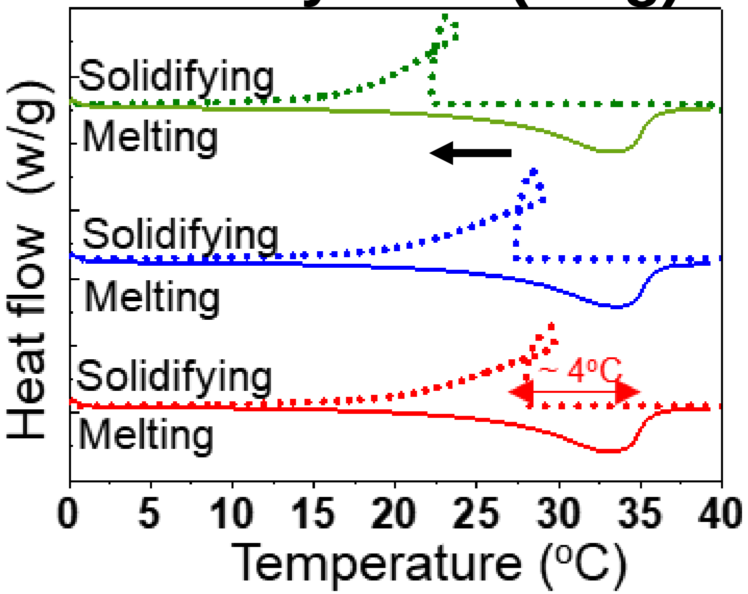




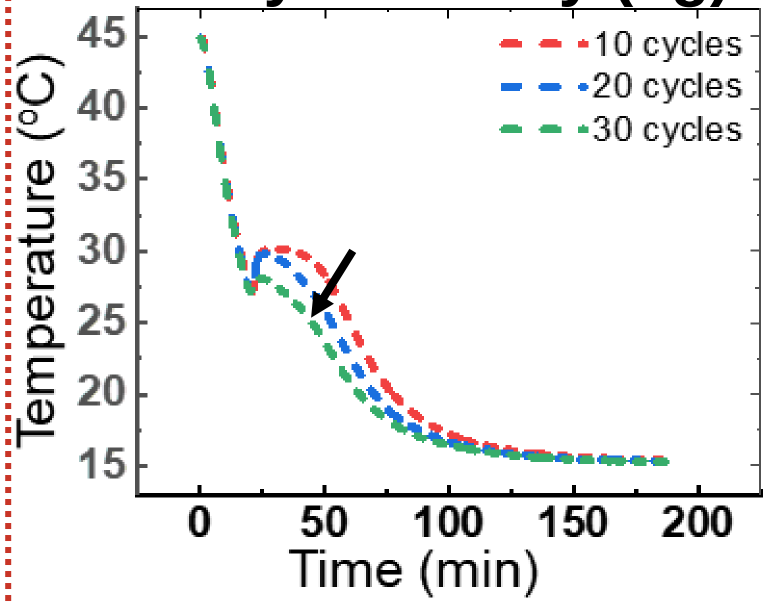
- At pH 7, glycine exists in its zwitterionic form, acting as a molecular template for the nucleation with interacting both ions.
- The molecules in the layer can arrange themselves in a way that promotes the formation of crystal nuclei, and the crystals can then grow on these nuclei.

Thermophysical properties of gly-SSD

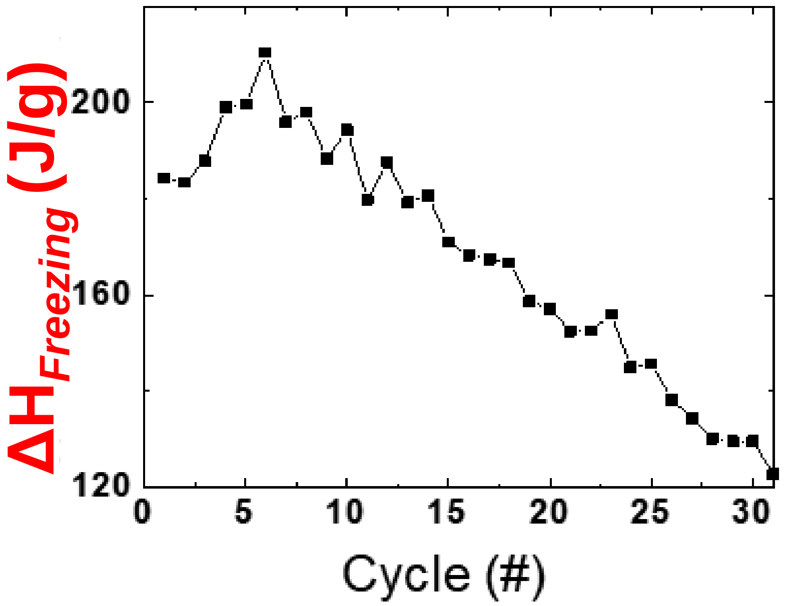
By DSC (~mg)



By T-History (~g)

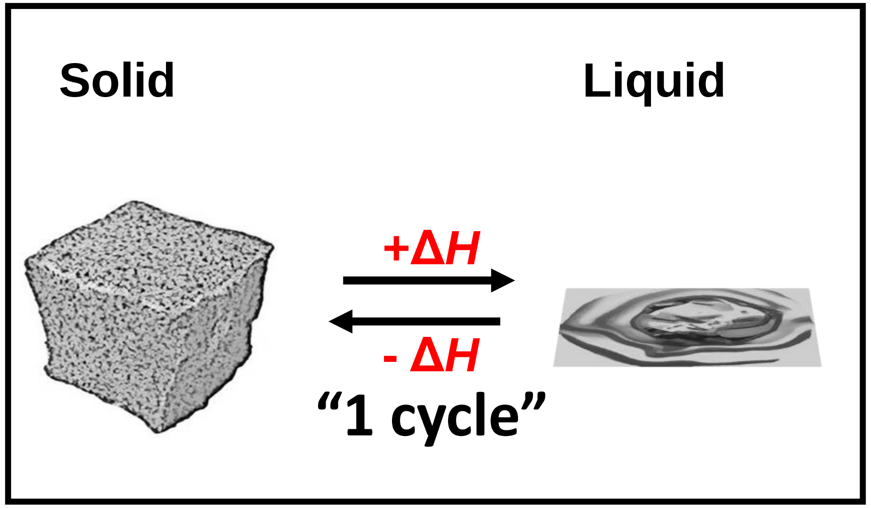


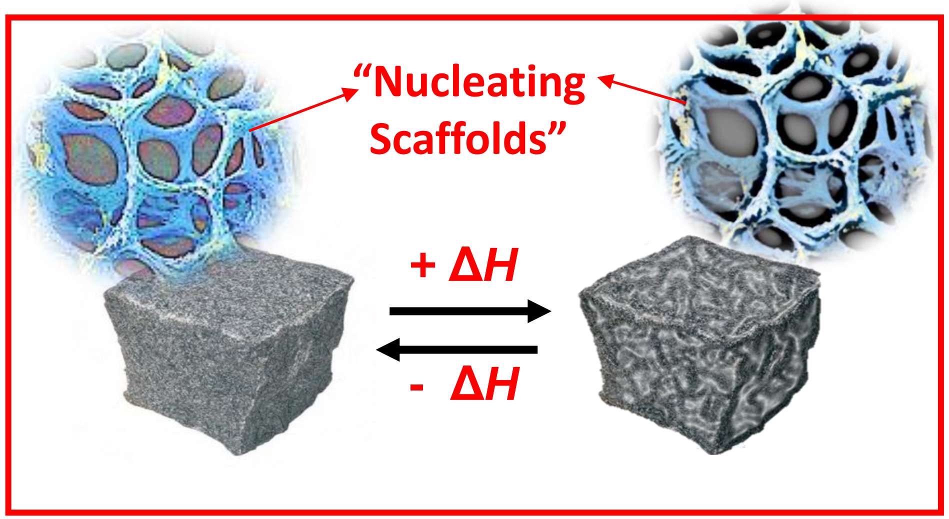
After cycles

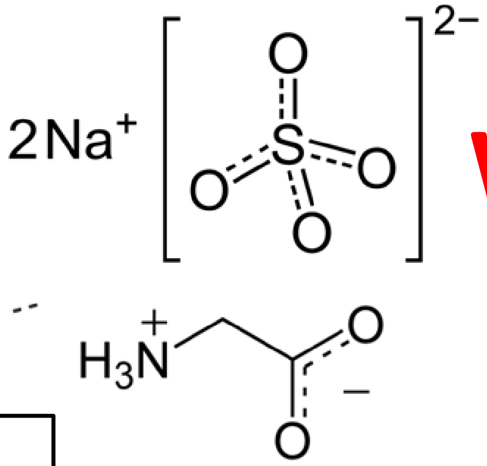


- zwitterionic nature of glycine allows for strong electrostatic interactions with the particles, which enhances the likelihood of nucleation and reduces supercooling
- **This is the first study that reports supercooling less than 4°C, demonstrating on both T-history and DSC**
- **However, the energy storage capacity is decreased upon cycling, due to phase separation**

Combination with “Hydrogel”







With

Hydrogel

Glycine- nucleated Sodium sulfate decahydrate

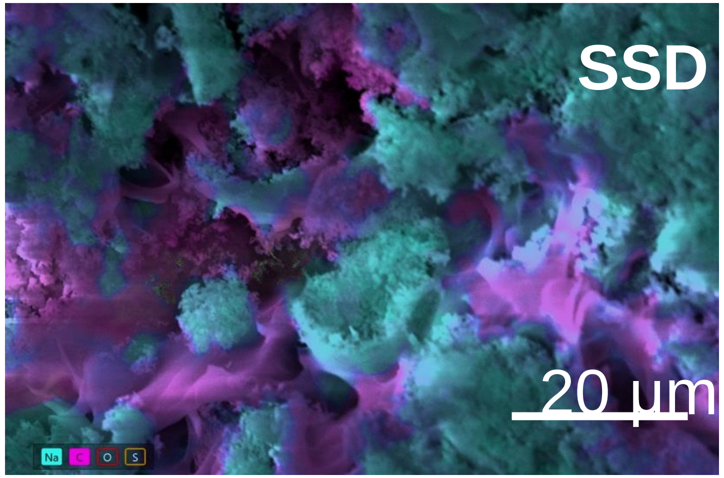
S.B Kang et al, To be submitted

US patent Application No. 63/495,434

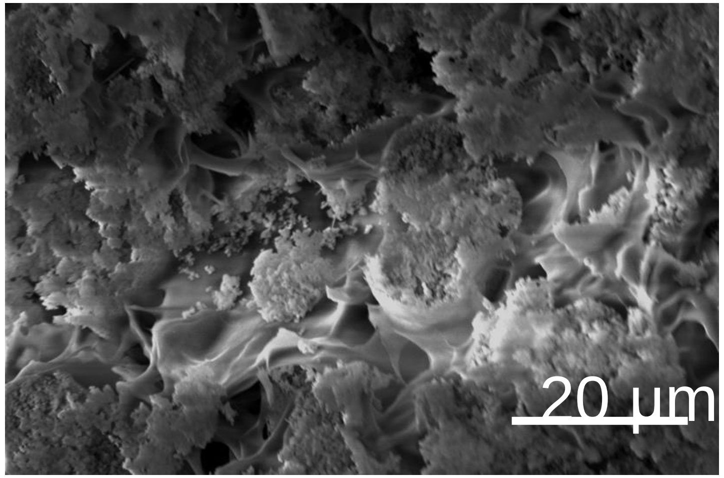
Gel-Glycine-nucleated Sodium sulfate decahydrate

"Confined" 3D network structure

- **<u>Gel</u>-**

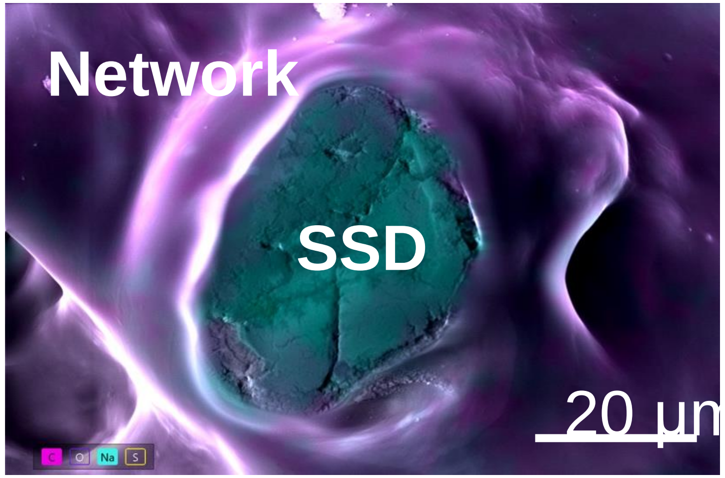


EDS mapping (Na->Green, Carbon->Purple)

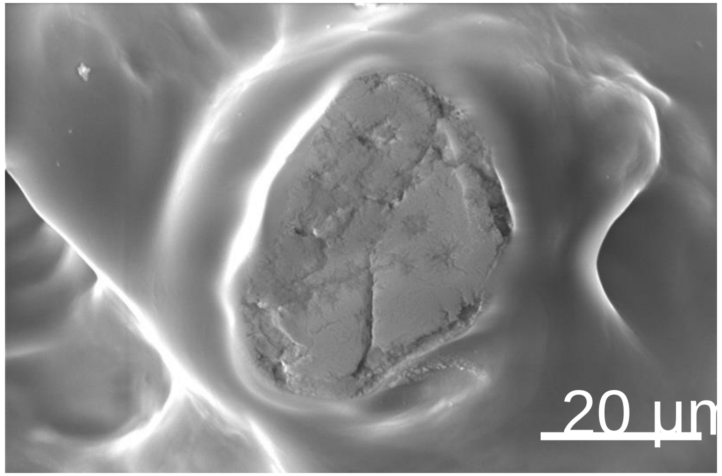


SEM image

- **Glycine-Gel-**



EDS mapping (Na->Green, Carbon->Purple)

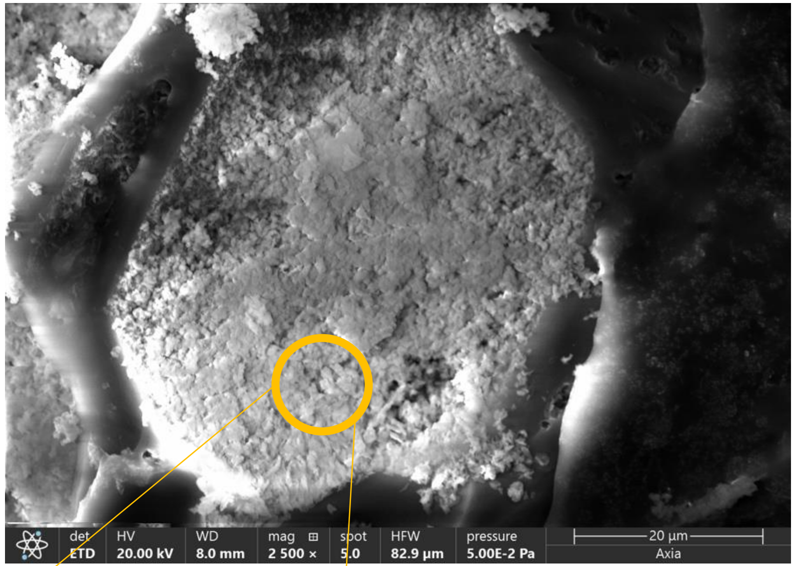


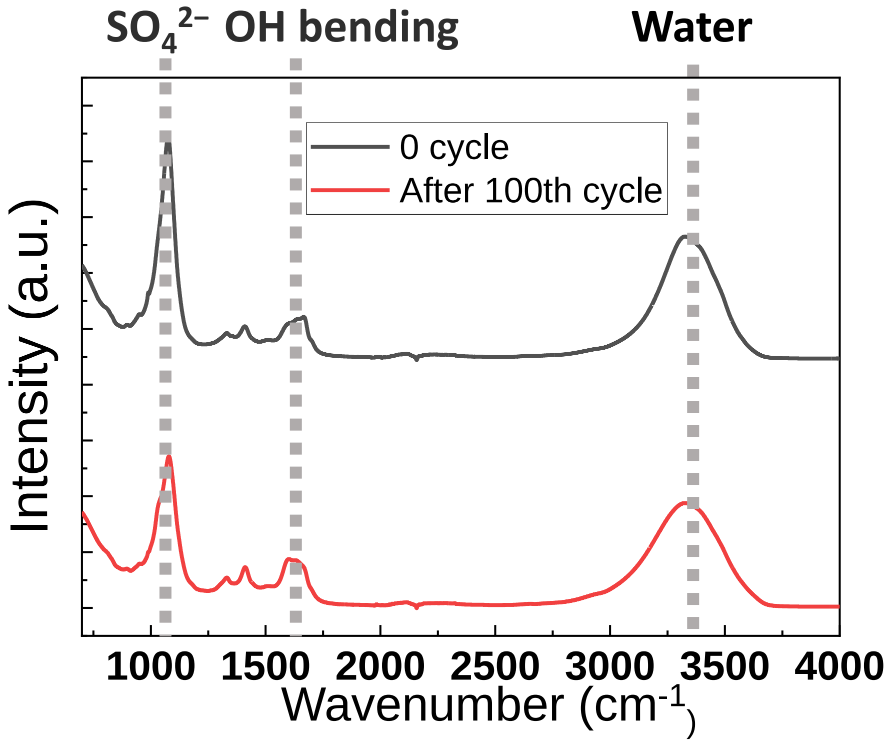
SEM image

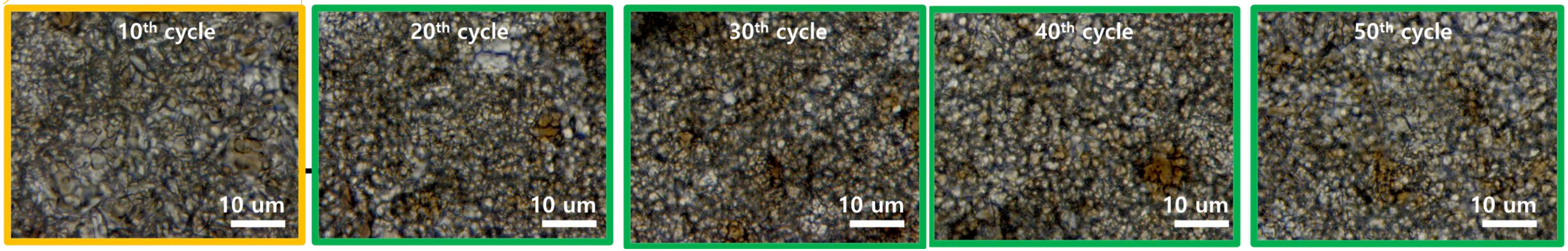
Role of Glycine:
- Nucleating agent
- Building block for 3d network structure

Thermocyclic Stability

After 100$_{th}$ cycle

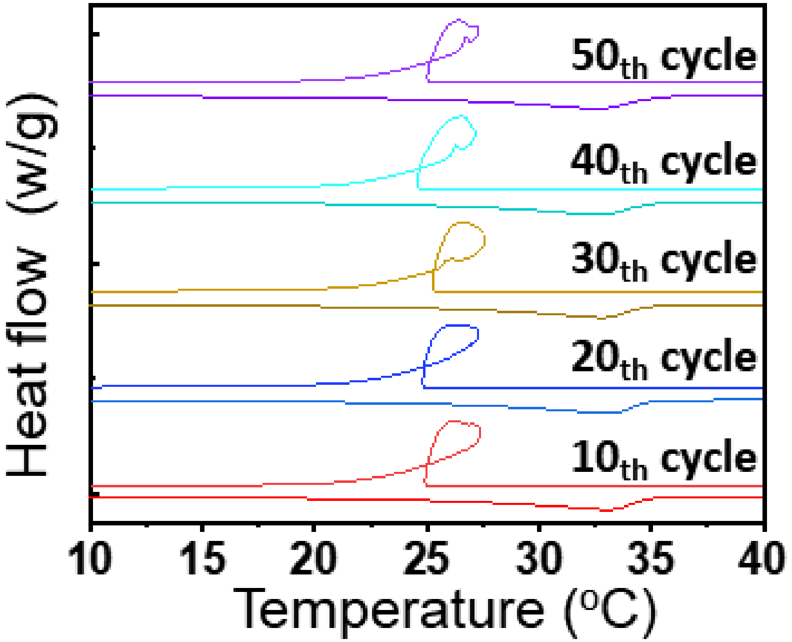




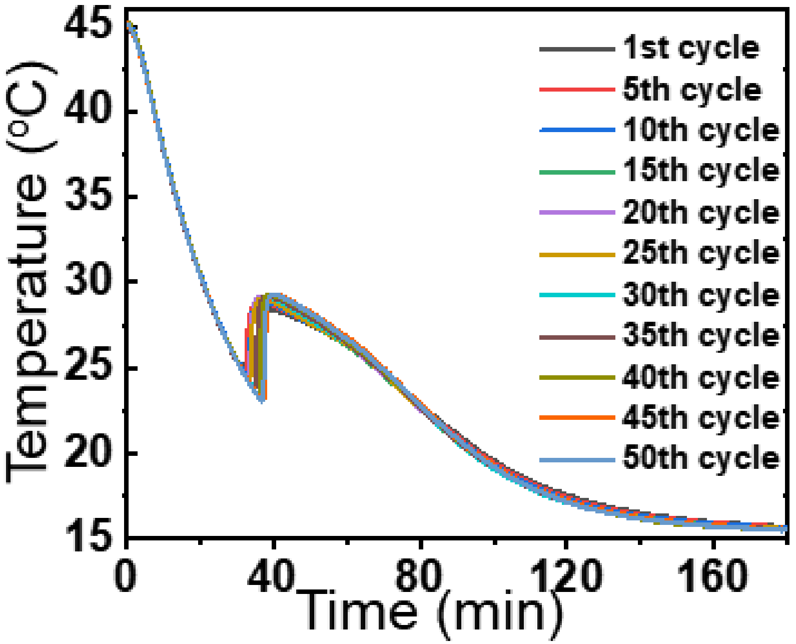


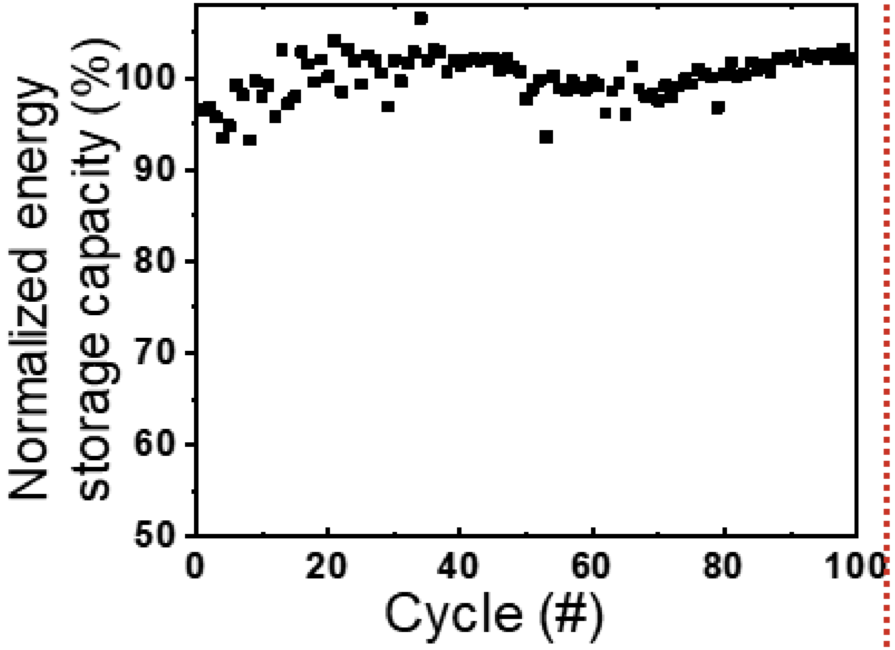
Thermophysical properties of composite

By DSC (~mg)



By T-History (~g)





- On-set temperature, stored energy density are maintained over cycles, indicating its excellent thermal stability.
- A 3D network composed of gel- Gly works perfectly for SSD.

Summary and Future Work

Summary

Gel-NA-SSD complex shows no degradation with thermal cycling (~100 cycles)

Supercooling reduced to ~5 C

No exotic materials or processing involved, cost expected to be reasonable

Scientific approach extends to other salt hydrates as well

Future Work

Focus on reducing supercooling further to 2 C and controlling variations

Focus on scaling gel fabrication

Focus on heat exchanger design and development

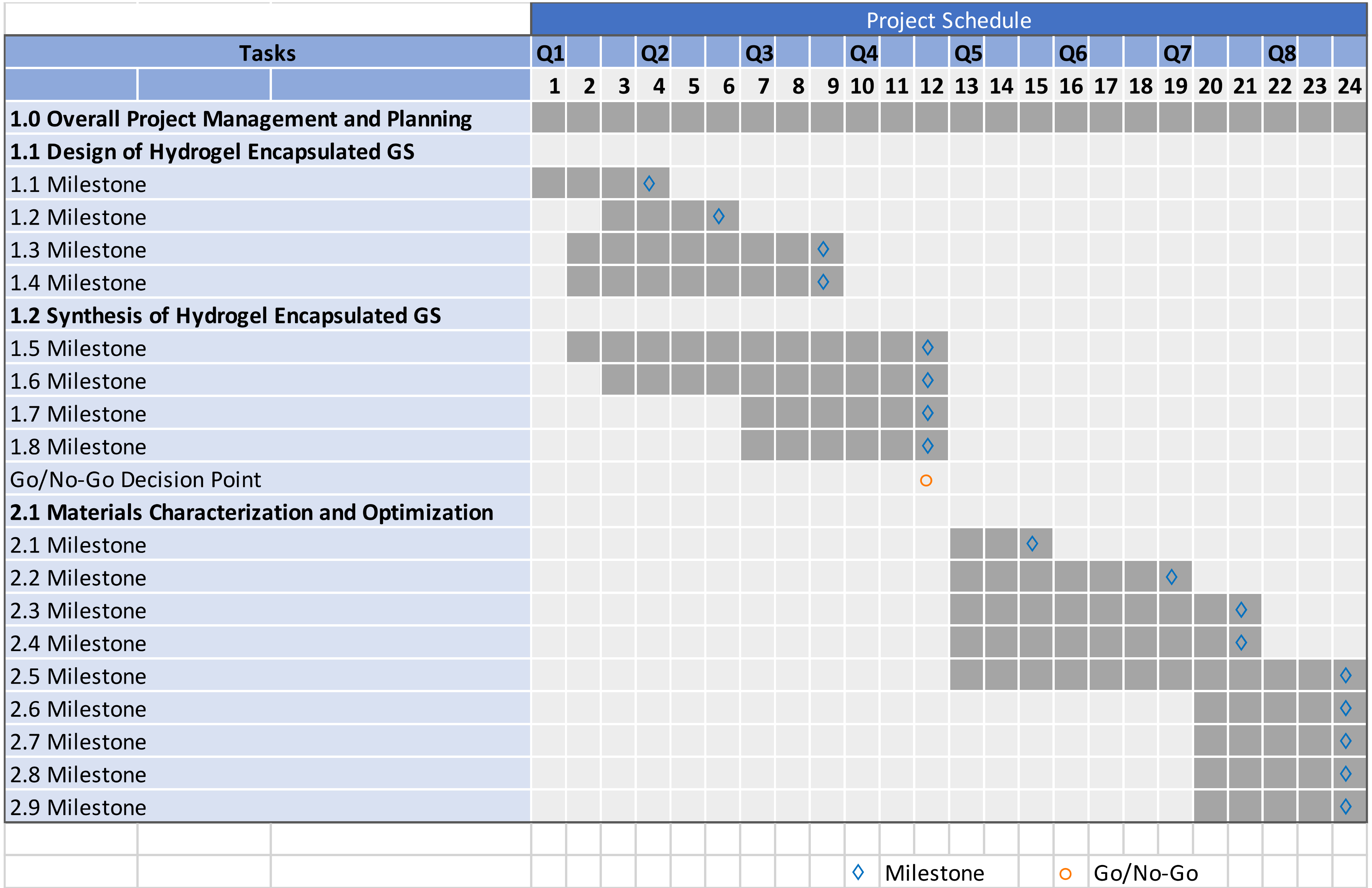
Market analysis for deployment in HP water heaters and other markets

Thank You

Performing Organization(s): University of Illinois, AO Smith
PI Name and Title: Sanjiv Sinha, Professor & Assoc. Head, Mechanical Science and Eng.
PI Email: sanjiv@illinois.edu
WBS #, FOA Project # and/or any other Project # DE-EE0009680

REFERENCE SLIDES

Project Execution



Team

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Chemistry and
Synthesis Lead

Nenad Miljkovic

Thermal Systems
and Simulations
Lead

Stephen Memory
Director, Corporate Technology

Tim Rooney
Project Engineer

Scaled-up materials characterization,
PCM in water heater systems,
Market identification,
TEA

2 Post-Docs: Dr. Sung Bum Kang, Dr. Jay Taylor

5+ Graduate Students