UC San Diego
Jacobs School of Engineering

GENERAL ENGINEERING AND RESEARCH

Low-cost Magnetocaloric Materials Discovery

Phase II STTR Project ID IN012

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Overview

Timeline

Phase I Project Start Date: 06/13/2016
Phase II Project Start Date: 07/31/2017
Phase II Project End Date: 07/30/2019

Barriers

H. High-Cost and Low Energy Efficiency of Hydrogen Liquefaction

Ultimate Target: Energy Required < 6 kWh/kg of LH2 at 300,000kg/day facility.

Budget

Total Project Budget: $1,150,000

- Phase I - $150,000
- Phase II - $1,000,000
- Total Phase II DOE Funds Spent: $761,211 as of 1/31/19

Partners

UCSD – Project Partner

US DOE – Project sponsor and funding

California Energy Commission – additional business development funding

Southern California Energy Innovation Network- Incubator for CleanTech companies

Interactions/collaborations

- Hydrogen Delivery Tech Team
- Other Industrial Collaborators – First Element, Camfridge, Haier, CoolTec-Applications.

Relevance

Objective: Develop low cost energy efficient magnetic refrigeration technology for hydrogen liquefaction.

- Hydrogen is cheaper and safer to transport and store in liquid form, but getting it into liquid form and keeping it in liquid form is not easy.

Barrier

H. High-Cost and Low Energy Efficiency of Hydrogen Liquefaction

- Energy required for H2 Liquefaction at point of production too high.
- Hydrogen boil-off from cryogenic liquid storage tanks needs to be minimized.

DOE Task

Explore new technologies.

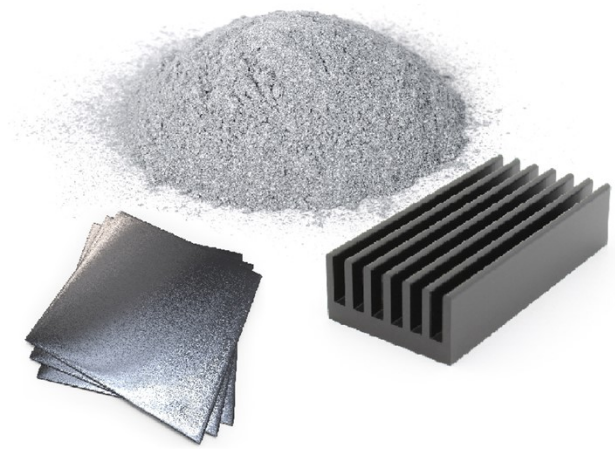
PNNL (J. Holladay) – building magnetic refrigeration H2 liquefaction prototype

GE&R Task

Discover, develop, and commercialize low cost high performance MCE alloys to enable magnetic refrigeration to move from prototype to production.

DOE Current Targets	FY 2015 Status	FY 2020 Target	Ultimate Target
Small Scale Liquefaction (30,000 kg H2/day)			
Installed Capital Cost ($)	70 million	70 million	-
Energy Required (kWh/kg of H2)	15	12	-
Large Scale Liquefaction (300,000 kg H2/day)			
Installed Capital Cost ($)	560 million	560 million	142 million
Energy Required (kWh/kg of H2)	12	11	6

Approach



Objective: Discover, develop, and commercialize low cost high performance MCE alloys to enable magnetic refrigeration to move from prototype to production.

Phase I Milestones - Completed

1.1 Discover low cost high performance MCE materials for sub 50K

Phase II Milestones

2.1 Discover novel MCE materials for >50K temperature applications **- Completed**

2.2 Optimize material synthesis processing to achieve:

a) High performance – need ΔT equivalent or better than Gd **- In Progress**

b) Low cost – Bulk selling price < $500/kg

c) High stability form - spheres or thin plates

2.3 Commercially Available MCE Products on www.geandr.com webstore **- Completed**

2.4 Prototype Model – New!

a) Small scale H2 Liquefaction to prevent boil-off losses at fueling stations – **- In Progress**

Approach

MCE material cost vs. Magnetic Field Cost

Lots of work on MCE Materials in last few decades

- No known commercial magnetic refrigerators yet for >4K applications.

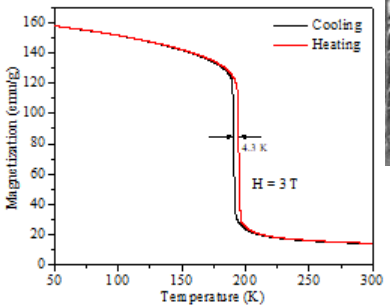
Traditional Approach to MCE Materials Research

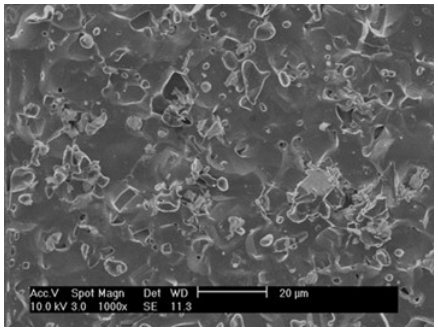
- Maximize ΔS
  - GdSiGe
  - LaFeSi
- Avoid rare–earth materials due to cost/availability
  - MnFeAs
  - NiMnSn

ΔS not a good measure of performance for 1st order materials.

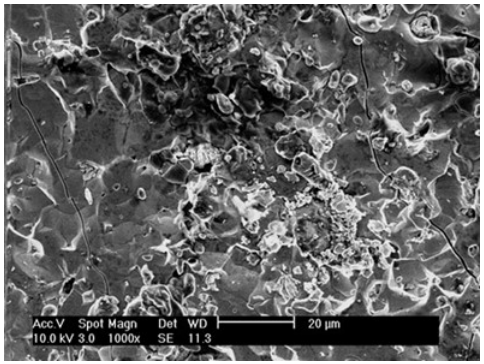
Performance is too low

LaFeSi
3T cycling
cracking observed





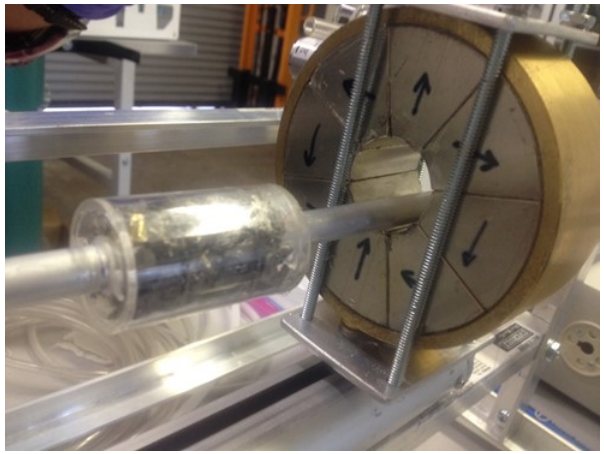
La-Fe-Si Before Magnetization



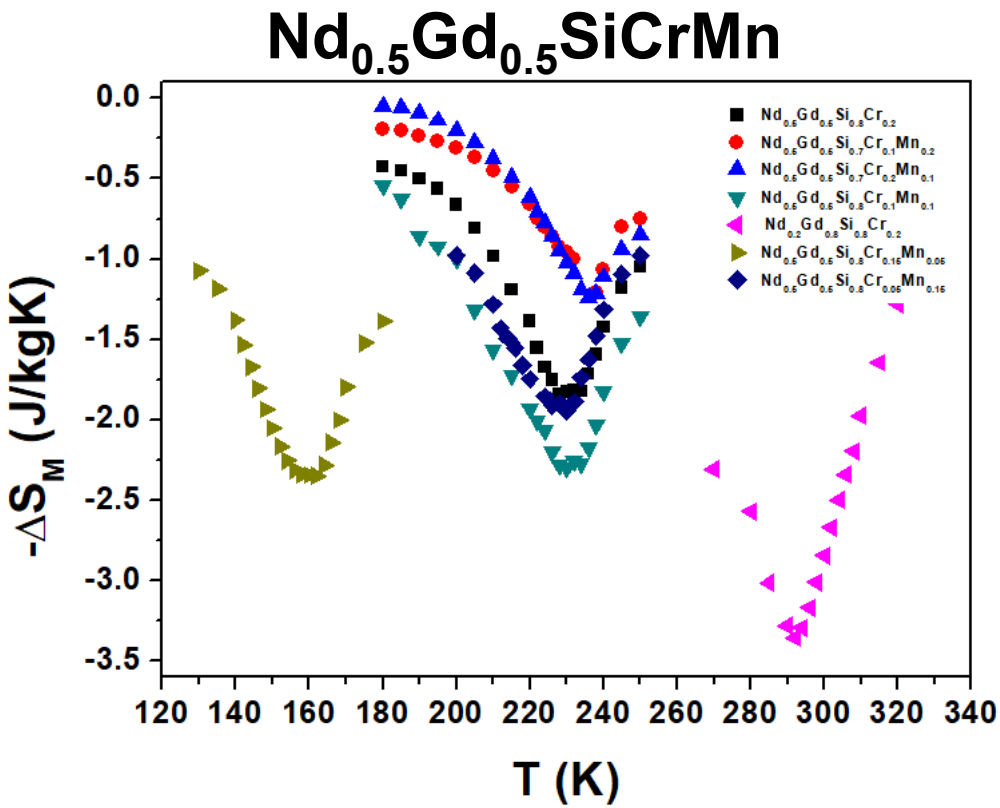
Magnetized in 30 cycles (0-3T, 100 Oe/s)

GE&R Approach to MCE Materials – stems from experience building magnetic refrigeration devices

- Materials with 2nd order only response
  - Maximize ΔT – high cooling power
  - Mechanically stable
- Use low cost rare-earth (Ce, Nd, Gd)
  - Need high performance to keep cost of Magnetic field reasonable



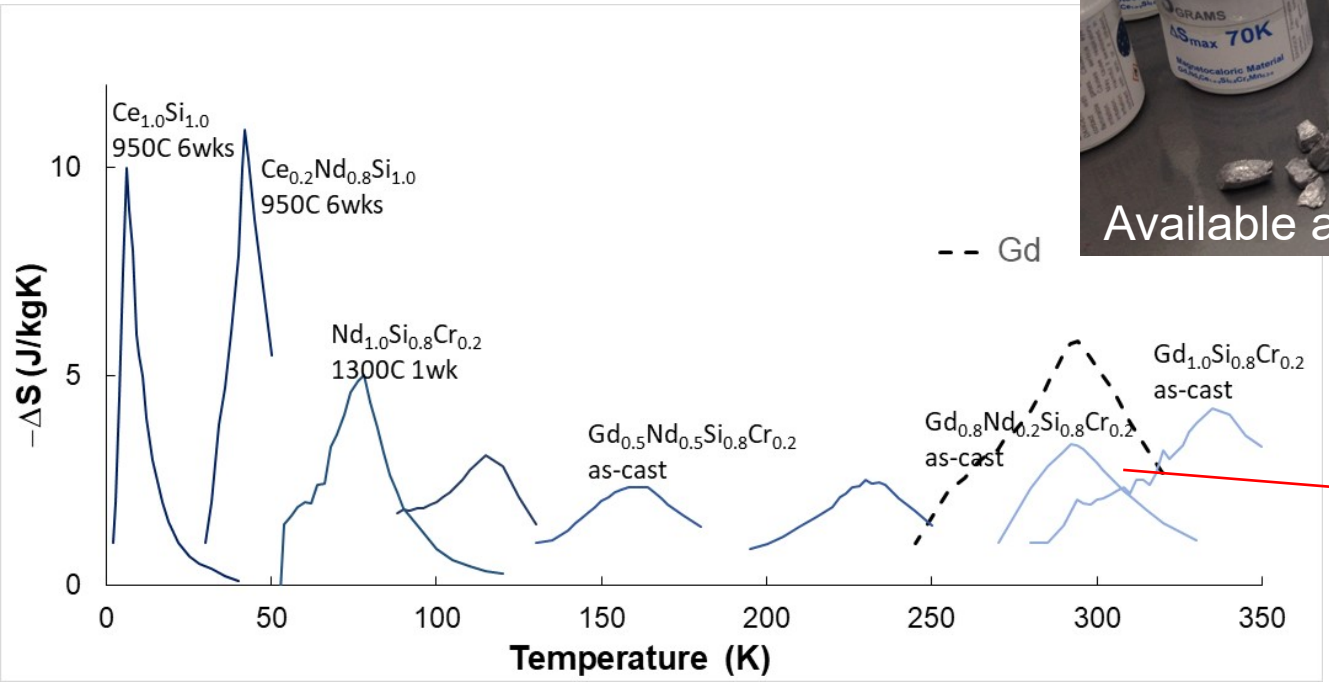
Accomplishments and Progress

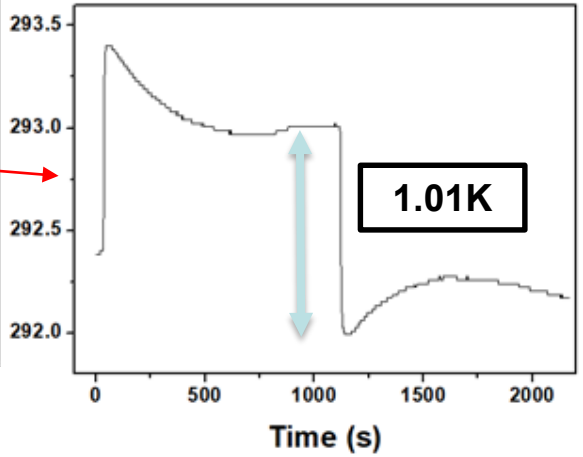


- Low cost 2nd order MCE compositions discovered for entire temperature range 9K – 325K
- Systematic doping performed to optimize performance
- Optimal doping concentrations discovered
- Doping with Cr found to significantly improve stability in air

Accomplishments and Progress

GE&R MCE materials performance at 3T field.





Lowest Cost and Highest Performance MCE Materials!

- Compositions with any Tc available between 9K – 330K
- Small quantities (5g) available for purchase at geandr.com
- Continued Development – Increase performance, Scale-up, optimization, custom forms

Accomplishments and Progress

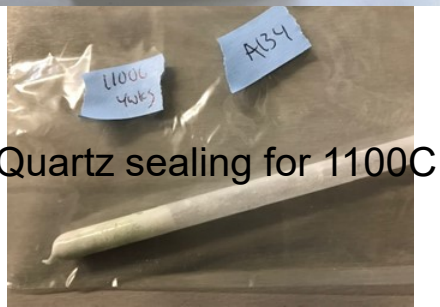
Increase Performance

- Different casting techniques evaluated to try to reduce/eliminate long anneals
  - Commercial casting companies
    - Arc melt
    - Induction melt
    - Arc melt/ rapid quench
    - Levitation casting / slow quench

Same performance after casting

- Bad news – no casting technique eliminates need for anneal
- Good news – for scale-up alloy casting can be done using any of these techniques
- Anneals required to achieve good MCE properties
  - Long anneals – logistical nightmare!
  - Higher temp – furnace $$$, oxidation

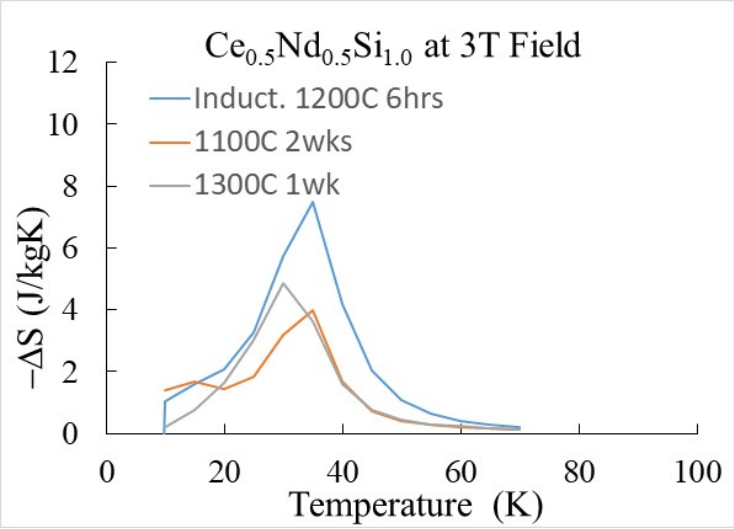
GE&R Furnaces

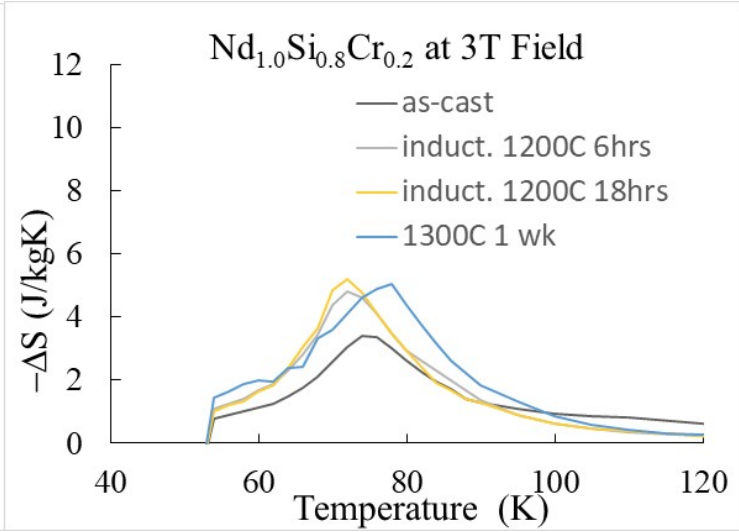


Quartz sealing for 1100C

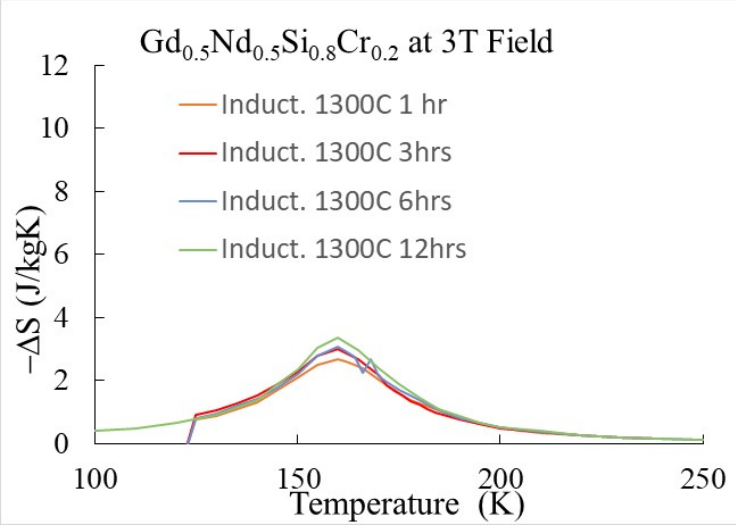
Accomplishments and Progress

Annealing Development





Element	Melting Temp (C)
Gd	1380
Nd	1021
Ce	800
Si	1414
Cr	1907



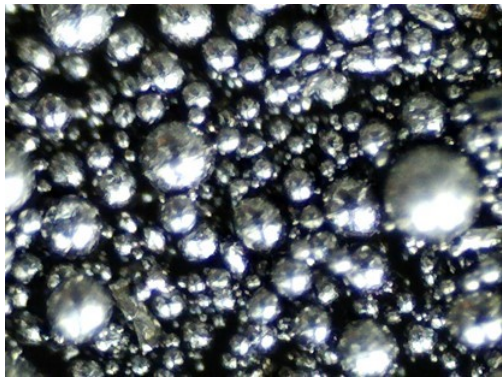
- Anneal time/temp must be determined for each composition.
- Higher temperature reduces anneal time
- Binary vs Ternary vs Quaternary
  - longer time to homogenize
  - CeSi, CeNdSi, NdGdSiCr
- Melting temp. varies
  - Cr – high temp
- Need higher temp furnace (1700C) for compositions with peak DS>70K

Binary	Melting Temp (C)
GdSi	1820
NdSi	1677
CeSi	1590
$Si_{0.8}Cr_{0.2}$	1400

Accomplishments and Progress

High Stability Form for MCE Materials

- Spheres - Rotating Disk Atomization – Arcast Inc. Toll service
  - turnaround time an issue
  - need to bring equipment in-house to achieve 1kg scale
- thin plates
  - too brittle to slice
  - hotpressing/sintering powder works great
  - need to bring hotpressing equipment in-house to scale



Hotpressed powder

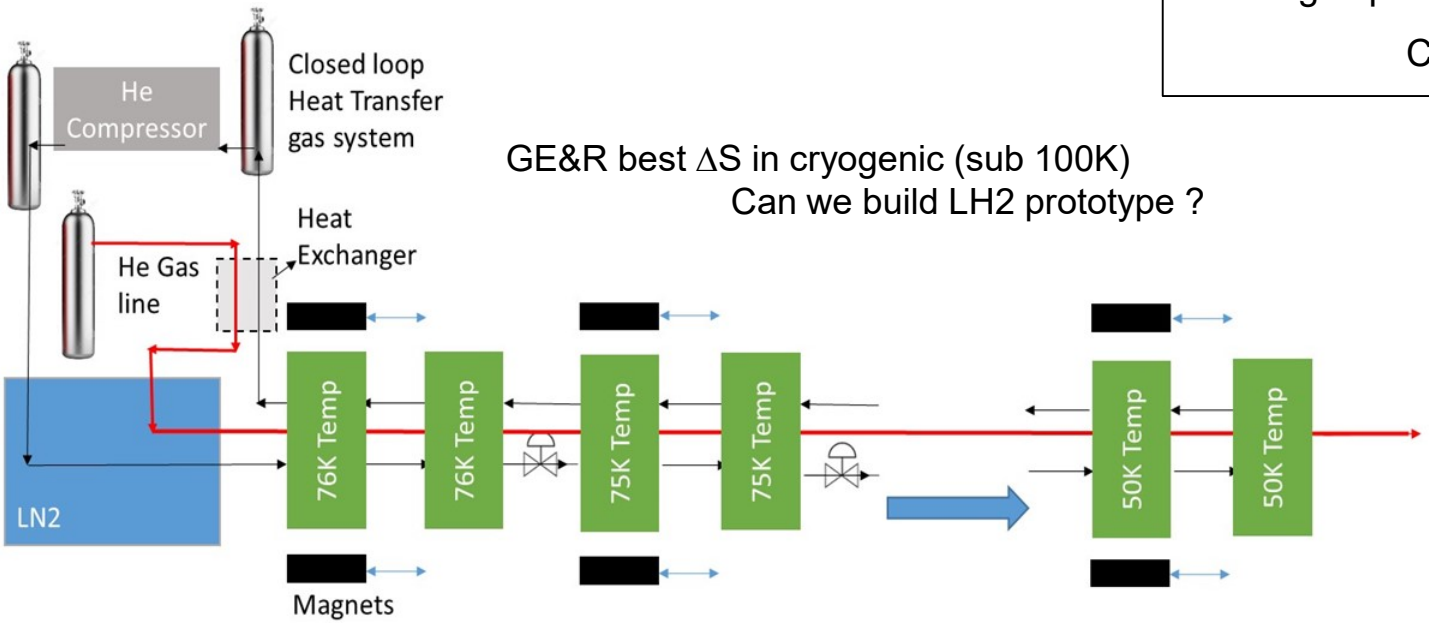
Accomplishments and Progress

Active Magnetic Regenerator Model

- GE&R material properties
- Permanent magnets

→ Model →

Mass flow for each stage
Material mass at each stage
Heat rejection at each stage
Cooling capacity at each stage
COP



GE&R best ΔS in cryogenic (sub 100K)
Can we build LH2 prototype ?

Modeling in progress to determine feasibility and design optimization for small scale H2 liquefaction system.

GOAL: 300kg/day H2 liquefaction system with >50% of Carnot Efficiency

Reviewer Responses

This project was not reviewed last year.

A Collaborative Project

Partner	Project Role
US DOE	Project sponsor and funding
University of California, San Diego (UCSD)	Project partner. Subcontractor. Assisting with materials development and optimization.
California Energy Commission (CEC)	Additional funding provided for business development through CALSeed Program. Participation in CleanTech Open business accelerator program.
Southern California Energy Innovation Network (SCEIN)	Networking incubator for CleanTech companies in Southern California. GE&R officially accepted into program. They provide network / mentor resources.
Hydrogen Delivery Tech Team	Annual reporting provided to HDTT
Other Industry Partnerships	In Progress – We have engaged the following entities: First Element, Air Liquid, Camfridge, CoolTec-Applications, Denso Corporation, Haier (GE Appliances).
Pacific Northwestern National Lab	Future partner – proposal pending to test PNNL proprietary heat treatment technique

Remaining Challenges and Barriers

Magnetic Refrigeration

For MCE Materials Commercialization:

- Performance targets for sub 70K compositions have been met/exceeded.
- Performance targets for >200K compositions need continued process development (higher temperature anneals) and optimization to hit performance targets.
- Commercialization – MCE materials market is mostly interested in RT applications.
    - Need to achieve higher performance on our RT materials
    - Need to scale-up to at least 1kg batches to supply R&D efforts
        - Additional development / equipment needed to scale

For Hydrogen Liquefaction:

- Both large scale magnetic refrigeration production plants and small scale magnetic refrigeration systems to prevent boil-off at point of use are needed.
- Only two known entities working on systems (Pacific Northwestern National Lab and Japanese National Institute of Material Science). Need industrial effort to move magnetic refrigeration technology forward.
    - Need to demonstrate small scale H2 liquefaction

Proposed Future Work

Remainder FY2019

Phase II Milestones	Description	Percent Complete
1	Discover MCE for >50K applications - Low cost compositions with 2nd order response to cover 9-300K range have been discovered that meet/exceed cost and performance requirements to be viable in all magnetic refrigeration applications.	100%
2	Optimize processing to achieve high performance, low cost, and stability. - Processing pathway for scale-up identified - New in-house equipment needed to achieve 1kg batches and spheres/thin plate forms. - For the remainder of Phase II, we will continue to optimize anneal processing to meet/exceed RT performance targets	90%
3	Commercially Available MCE Products on www.geandr.com webstore. - Small quantities available for purchase.	100%
4	Prototype – New! - Modeling in progress to evaluate feasibility and optimize design for small scale H2 liquefaction to prevent boil-off at fueling stations. - By end of Phase II we intend to have optimal design determined from model.	50%

Any proposed future work is subject to change based on funding levels.

Proposed Future Work

Potential Phase IIA/IIB

- A proposal is pending to the California Energy Commission for funding to scale-up our MCE materials production line.
- A proposal is pending to the DOE which is a collaborative effort between GE&R and PNNL to develop new heat treatment technique to reduce MCE materials processing time/cost.
- We will apply for Phase IIA/IIB funds in April 2019 to accomplish Milestone 2 and 3 outlined below.

New Milestones	Description
1	MCE Materials Scale-up - Install equipment and develop procedures to accommodate 1kg/day production; - Work with PNNL to develop new heat treatment technique to reduce processing time/cost; - Develop in-house processes to form MCE materials into spheres and thin plates; - Optimize processing to meet at scale cost and performance requirements.
2	Build Small Scale Cryogenic Magnetic Refrigeration System - Based on Phase II modeling results, build a magnetic refrigeration system, which cools Helium from 77K to 65K using GE&R MCE materials and only permanent magnets. - Purpose – to demonstrate small scale cryogenic cooling ability of technology.
3	Build 300kg/day H2 Liquefaction Prototype with COP>50% - Application – Low energy solution to prevent boil-off losses at fueling stations

Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities

Additional Funding Received

- CALSeed Grant from the California Energy Commission is supporting business development activities for our Magnetic Refrigeration technologies.

Potential Future Funding

- Applied for DOE funding for a collaborative effort between GE&R and PNNL to develop new heat treatment technique to reduce MCE materials processing time/cost.
- Applied for California Energy Commission funding to scale-up our MCE materials to a 1kg/day production line and form materials into spheres/ thin plates.
- We will apply for Phase IIA/IIB funds in April 2019 to build a small scale cryogenic magnetic refrigeration system with the purpose of demonstrating small scale H2 liquefaction.
- Industrial Funding Sources – In progress.

Patents

- PCT application (US2018/012836) filed in Feb 2018 for our ternary based compounds. We will enter national stage (US, Japan, Europe, China) in July 2019.
- PCT application (US 62/634078) filed in Feb 2019 for our >50K MCE compositions

Summary Slide

- MCE Materials available for purchase in small quantities, 2nd order, any temp. 9-330K.
  - Webstore www.geandr.com

- Scale-up
  - Processing path for scale-up and formation of spheres/thin plates has been identified and equipment tested and verified for compatibility with our compositions.
  - Additional equipment will need to be brought in-house and process development effort will be needed to achieve 1kg/day scale to accommodate customer magnetic refrigeration prototype development.

- Modeling results for small scale H2 liquefaction system look promising.
  - Magnetic Refrigeration may be able to provide a low cost and low energy solution to prevent boil-off losses at fueling stations – this is a key issue which must be addressed to achieve $3/kg H2@scale retail price.

Technical Back-Up Slides