
Low-Cost Magnetocaloric Materials Discovery

Robin Ihnfeldt (Primary Contact), Renkun Chen
(University of California San Diego), Sungho Jin
General Engineering & Research
10459 Roselle St. Ste. A
San Diego, CA 92121
Phone: (858) 736-5069
Email: rihnfeldt@geandr.com

DOE Manager: Neha Rustagi
Phone: (202) 586-8424
Email: Neha.Rustagi@ee.doe.gov

Technical Advisor: Sungho Jin
Phone: (858) 945-2030
Email: Jin1234jin@gmail.com

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Overall Objectives

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

Fiscal Year (FY) 2018 Objectives

- Discover low-cost magnetocaloric materials which function at temperatures greater than 50K.
- Characterize ΔT of materials and confirm second-order response.
- Optimize composition and processing to achieve high-performance (ΔT equivalent or better than gadolinium [Gd]), low-cost (target <\$400/kg at large scale), and high-stability form useful for magnetic refrigeration (spheres and/or thin plates).
- Commercialize magnetocaloric materials products on www.geandr.com webstore.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

(H) High-Cost and Low Efficiency of Hydrogen Liquefaction.

Technical Targets

The transportation and storage of hydrogen is safer and more economical when it is in liquid form, but getting it into liquid form and keeping it in liquid form is not easy. Despite significant efforts to improve compression-based liquefaction systems, they remain too inefficient and expensive to meet the DOE hydrogen production and delivery targets shown in Table 1. Therefore, exploration of new refrigeration technologies—such as magnetic refrigeration—is needed.

General Engineering & Research (GE&R) is supporting the DOE effort to develop magnetic refrigeration technologies for high-efficiency hydrogen liquefaction. Our goal is to discover, develop, and commercialize low-cost high-performance magnetocaloric effect (MCE) alloys to enable magnetic refrigeration to move from prototype to production. Targets for our MCE materials have been defined as follows:

- Cost: \$400/kg or less, at large scale
- Performance: Equivalent or better than Gd ($\Delta S \geq 6$ J/kg K in 3T field)
- Forms: Sub-mm sized spheres and thin plates.

FY 2018 Accomplishments

- Discovered low-cost MCE material set with novel second-order response for temperature range 9–340 K.
- Increased performance for sub-80 K MCE materials from $\Delta S \sim 4$ J/kg K in 3T field (Phase I) to $\Delta S \geq 10$ J/kg K in 3T field, which exceeds the project targets.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Measurable ΔT verified at room temperature and consistent with second-order response.
- In-house small-scale manufacturing processes set up, with initial line of MCE materials products commercialized on www.geandr.com webstore.
- Alloys tested on rotating disk atomization process, with sub-mm sized spheres obtained and MCE properties maintained.
- Discovered that compositional doping improves both MCE performance and material stability in air.

Table 1. DOE Hydrogen Liquefaction Technical Targets

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 H ₂)	15	12	—
Large-Scale Liquefaction (300,000 kg H₂/day)			
Installed Capital Cost (\$)	560 million	560 million	142 million
Energy Required (kWh/kg of H ₂)	12	11	6

INTRODUCTION

Magnetic refrigeration utilizes the MCE, which is the temperature variation of a magnetic material after exposure to a magnetic field (see Figure 1) [1]. The MCE is an intrinsic property of a magnetic solid. The thermal response of the MCE material to the application or removal of a magnetic field is typically maximized when the material is near its magnetic ordering temperature, also known as the Curie temperature (T_c). The useful portion of the MCE usually spans about 25 degrees on either side of the material's T_c [2]. Therefore, to span a wide temperature range, a refrigerator must contain several different MCE materials arranged according to their T_c .

There are several issues that must be solved before the technology of magnetic refrigeration can move forward from prototypes to mass production. One of these issues is the lack of commercially available low-cost MCE materials that will function—for a long period—in a magnetic refrigeration environment, such as the active magnetic regenerator (AMR), which is being developed by several entities [3–7]. Synthesizing MCE materials is not easy, and the known materials are expensive rare-earth based or poor performance. Our goal is to discover, develop, and commercialize low-cost, high-performance magnetocaloric alloys to enable magnetic refrigeration to move from prototype to production.

APPROACH

The MCE occurs due to either a second-order phase transition (magnetic), or a first- and second-order phase transition (structural and magnetic, respectively). Materials with second-order transitions are entirely reversible, and materials with first-order transitions are not. Over the last two decades, the approach to MCE materials development has been to maximize entropy change (ΔS) and to reduce or eliminate rare-earth materials from the composition. Materials such as GdSiGe-, LaFeSi-, and MnFeAs-based alloys have been discovered that exhibit a giant magnetocaloric effect (large ΔS), but it is due to a first-order phase transition. In previous work, our team synthesized many of the known MCE materials and built MCE devices. We found major issues occur when using MCE materials with first-order transitions, including low ΔT and cracking due to volume changes when exposed to numerous magnetization cycles [8]. We also found that MCE materials without a rare-earth component were useless in actual devices because their performance was too low. Based on this experience, our approach to discovering better MCE alloys included the following requirements: (1) only second-order response, and (2) use low-cost rare-earth elements (Ce, Nd, Gd) to keep costs reasonable while still maintaining high performance. CeSi ($T_c \sim 9$ K) and NdSi ($T_c \sim 45$ K) alloys with second-order only MCE properties were reported by two different groups a few years ago [9, 10]. During Phase I, we synthesized ternary compounds of $Ce_xNd_{1-x}Si$ where $0 < x < 1$ and showed high performance MCE properties from 10 K to 45 K [11]. Our Phase II approach has been to systematically test compositional and processing effects on this alloy set to achieve functionality at higher temperature ranges, and demonstrate large-scale manufacturability.

RESULTS

During FY 2018 we systematically synthesized and characterized hundreds of alloys of various compositions. Figure 1a shows the interesting results of doping of the $Nd_{1.0}Si_{0.9}M_{0.1}$ where M is Fe, Cu, Co, Ni, Zn, Cr, Mn, Sn, and Al. With replacement of the silicon with Fe, Cu, Co, Ni, Zn, and Cr, the T_c was increased to ~ 75 K, and replacement with Mn increased T_c to ~ 125 K. Synthesis and characterization of $Gd_{1.0}Si_{0.8}Mn_{0.1}$ (Figure 1b) showed T_c of ~ 340 K, and similar to the Phase I Ce-Nd-based compounds, it was discovered that variation in the T_c from 125 K to 340 K can be achieved by varying the Nd-Gd concentration. From this discovery, we now have a novel MCE material set with second-order only response that uses only low-cost elements and has functionality over the entire temperature range, 9–340 K. A new patent application has been filed to cover the novel compositions discovered this year.

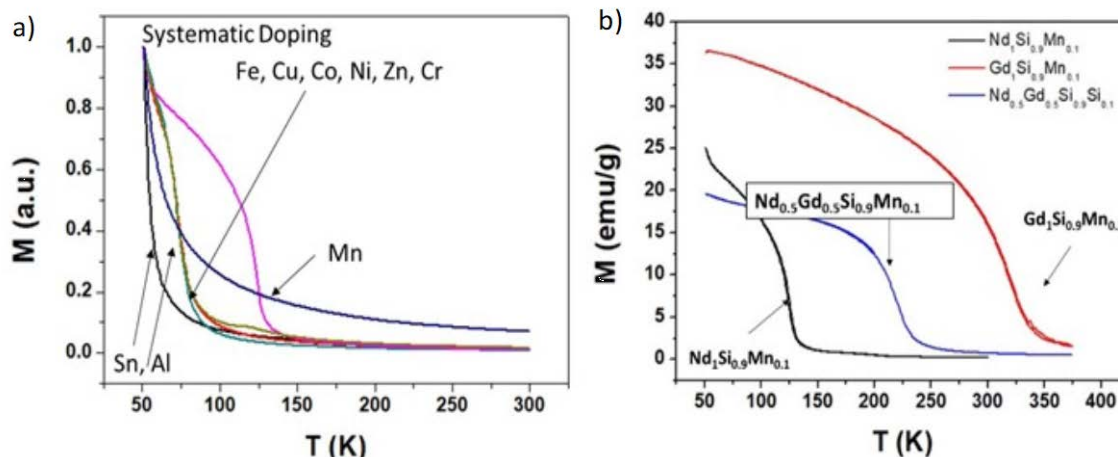


Figure 1. Magnetization versus temperature for (a) $Nd_{1.0}Si_{0.9}Mn_{0.1}$ compounds, where M is Fe, Cu, Co, Ni, Zn, Cr, Mn, Sn, and Al; and (b) Nd-Gd based compounds.

Effects of composition on MCE performance was tested. Figure 2 shows the change in entropy (ΔS) versus temperature for various compositions with different doping concentrations and elements. Thus far, the best performance is achieved with replacement of 20 at% of the Si with Cr or Mn, or some combination of these elements. Error on the ΔS measurements is ± 0.5 J/kgK.

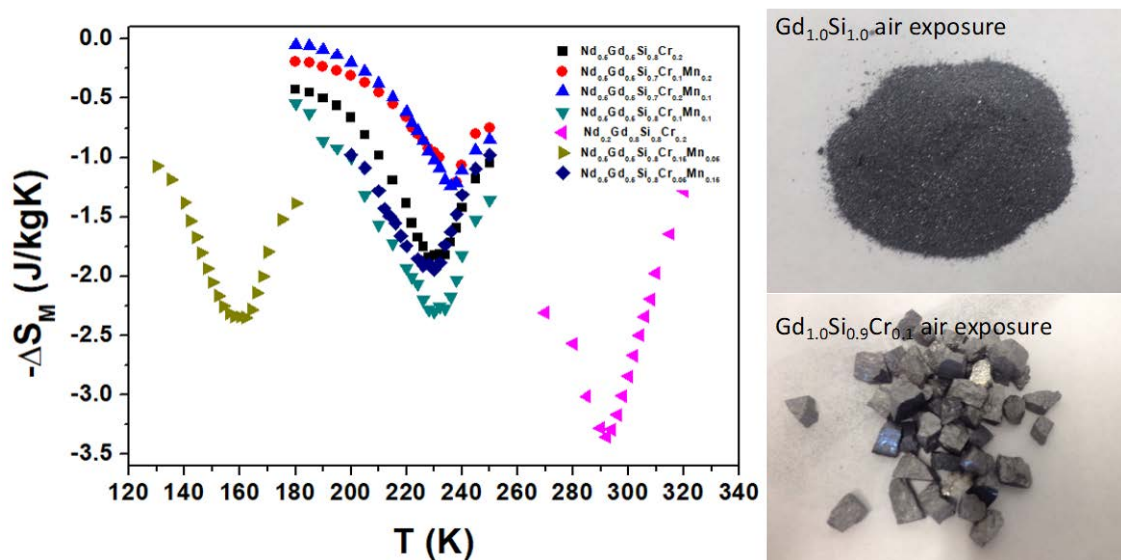


Figure 2. ΔS versus temperature for various magnetocaloric compositions. Images show presence of Cr eliminates long-term oxidation degradation of MCE materials with exposure to air.

X-ray diffraction (XRD) data (Figure 3) indicates the optimal performance may be due to a dual structural phase occurring at the 20 at% concentration, as only single phase occurs with higher or lower concentrations. Interestingly, the MCE properties (T_c and peak ΔS) are affected similarly with doping of Cr or Mn, where either element can be used to achieve desired T_c and peak ΔS performance as long as the 20 at% composition is maintained. The materials stability in air is significantly improved with presence of Cr, however, which is not the case with Mn. Compounds with no Cr after several weeks of exposure to air slowly degraded to an oxidized powder, whereas alloys with Cr showed little to no oxidation when exposed to air (see Figure 2). Many of the currently available or known MCE materials also degrade with exposure to air, and thus must be handled only in inert atmospheres, which makes it much more difficult to build systems. The ability to provide

MCE materials that are stable in air at room temperature is a major improvement that will significantly lower the cost and time needed to develop devices. Further, testing of other elemental doping to improve performance is in progress.

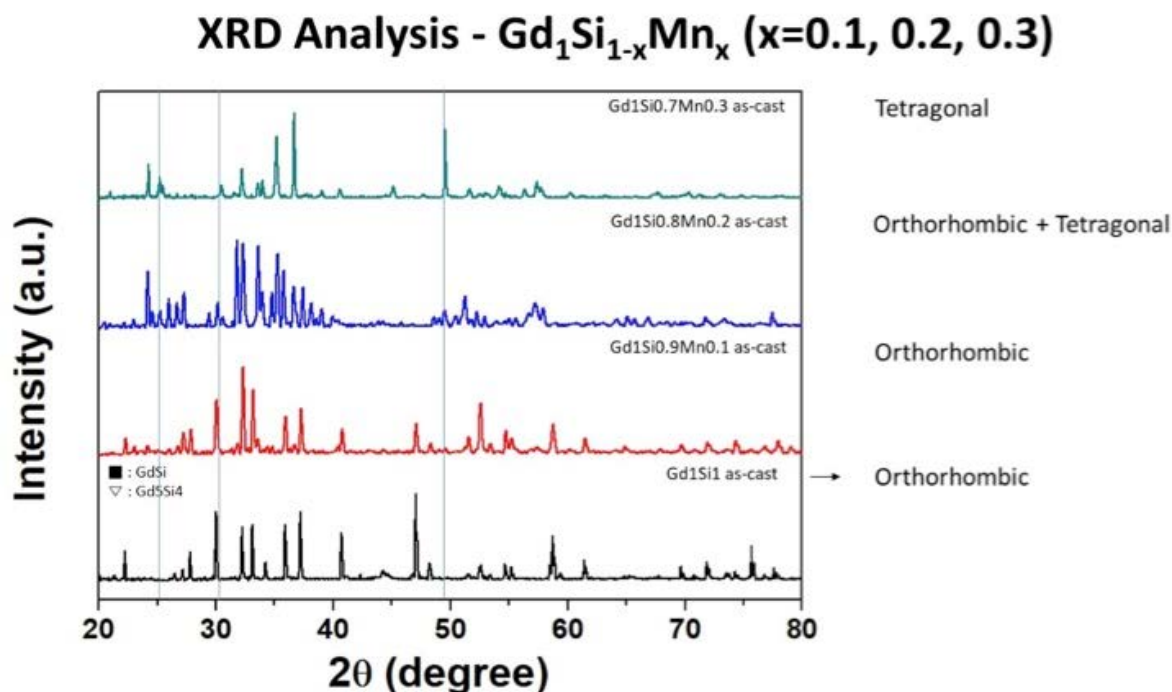


Figure 3. XRD data for various magnetocaloric compositions

Effects of processing on MCE properties also has been investigated. The alloys can be formed using a number of different melting techniques. An arc melt process is economical for quickly synthesizing small quantities of alloys. However, arc melt furnaces operate at $>5,000^\circ\text{C}$ temperatures, which often leads to evaporative loss of material. This loss can be difficult to control, thus batch-to batch-variation is significant. We have installed an induction melt system, which shows good performance can be achieved with this technique. Temperatures during induction melting are better controlled, and typically $<2,000^\circ\text{C}$, which eliminates the possibility of evaporation losses. The challenge with induction melting is finding compatible crucibles and casting processes for rare-earth metals. In our current setup, we are able to enclose the material in tantalum foil during melting to achieve the desired alloy, however this is not practical for large-scale manufacturing. There also may be benefits to rapid quenching of the alloys. Both arc melt and induction melt systems are available for large-scale manufacturing. We are currently working with several alloy manufacturers that have both types of equipment available along with several different casting and quenching techniques.

Figure 4 shows the current best performance (ΔS) of GE&R material set versus temperature. Figure 4 also shows a ΔT measurement of our MCE material with peak performance near room temperature. The ΔT measurement was performed in air, using a thermal couple attached to a ~ 10 -gram piece of MCE material and magnetic field generated by a 1T Halbach Array magnet. The $\Delta T \sim 1^\circ\text{C}$ is consistent with a second-order reversible response. Aside from elemental Gd, which only works at room temperature, we believe our materials are the highest performance (largest ΔT) commercially available. They are the only materials on the market with functionality below 180 K, the only materials on the market that are supplied with certificate of analysis verifying performance (ΔS versus T), and the only materials on the market with second-order-only transitions (totally reversible and no cracking issues).

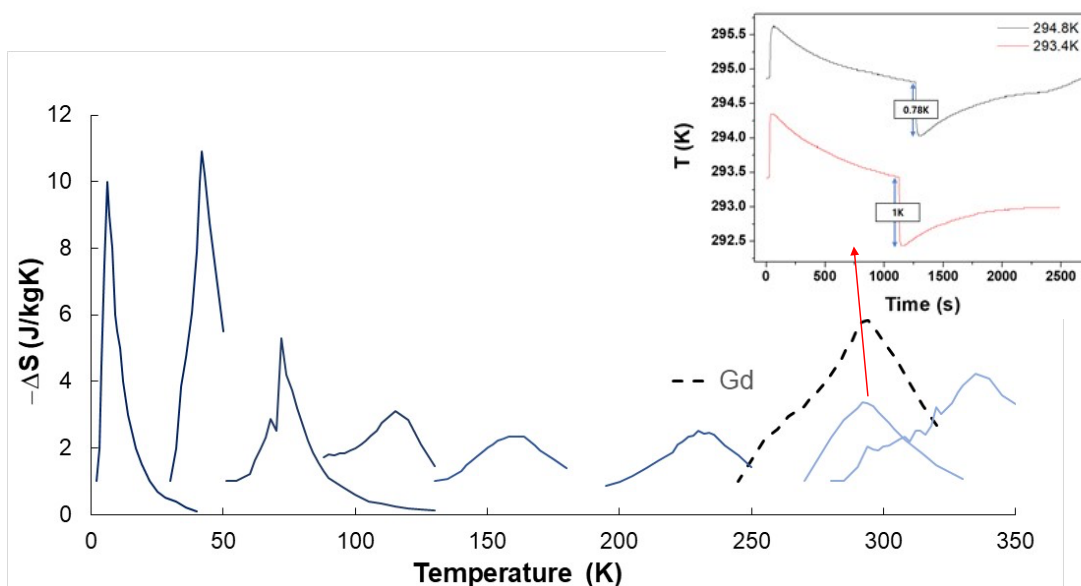


Figure 4. GE&R magnetocaloric materials performance (ΔS) versus temperature at 3T magnetic field (inset is ΔT measurement of GE&R room temperature composition with exposure to 1T magnetic field)

The intent of making these materials available as soon as possible is to allow other entities in R&D to begin testing and working with the materials, and potentially to provide us feedback on performance or other issues we need to address. The materials with working temperature below ~ 80 K show the highest performance with $\Delta S > 10$ J/kg K, which exceeds our target performance (that of Gd). The high performance was obtained by annealing the materials at 950°C for 6 weeks. The materials with working temperatures of more than 80 K are also in process of annealing, which we expect to improve performance. However, these long high-temperature anneals are expensive and time consuming. The anneals act to homogenize the materials, whereas phase separation during cooling may be occurring. We are investigating different casting and quenching techniques with several alloy manufacturers to see if this will allow reduced anneal time or eliminate the need for anneals altogether.

Initial feedback from potential customers of our MCE materials includes a request to form these materials into various shapes. We currently only are selling these in 5-g quantities in the form of small pieces (3–5 mm). Shapes such as sub-mm sized spheres, thin plates, and large ingots have been requested. Working with Arc Cast, Inc., we were able to successfully synthesize sub-mm sized spheres using their rotating disk atomization process [11]. The initial composition showed no degradation in performance. Additional compositions need to be tested on this process to ensure the higher-performance materials continue to maintain high performance. Processing optimization also needs to be done to better control the spherical size distribution. Formation of larger ingots (>500 g ingot) is in process, and machining into thin plates will be tested once large ingots with good MCE performance are successfully formed.

CONCLUSIONS AND UPCOMING ACTIVITIES

This project has made progress towards the ultimate goals of increasing the efficiency and reducing the capital cost of hydrogen liquefaction. In FY 2018 we have made progress along the critical path in support of developing magnetocaloric refrigeration technologies in that we have:

- Discovered a magnetocaloric material set that meets the target cost and has functionality over the entire temperature range from 9 K to 340 K

- Optimized composition and processing to exceed target performance for materials that function below 80 K
- Developed multiple synthesis pathways to achieve large-scale manufacturing goals
- Commercialized initial line of magnetocaloric materials on our webstore
- Demonstrated compatibility of rotating disk atomization process to form sub-mm sized spheres.

Upcoming activities will include:

- Continued investigation of compositional variation to improve performance
- Work with different alloy manufacturers to investigate effects of various casting and quenching techniques to improve performance and reduce anneal time
- Work with different alloy manufacturers to provide larger-scale manufacturing of ingots (>500 g/batch)
- Optimize rotating disk atomization process for narrower sub-mm sized distributions and meet cost targets
- Develop methods to form materials into thin plates.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. Awarded a Phase I CALSeed grant from the California Energy Commission for business-development efforts of magnetocaloric technologies.
2. Awarded “Best Emerging Technology” in the Western Region Cleantech Open Competition.
3. Accepted into the San Diego Regional Energy Innovation Network, which is an incubator/accelerator program for clean technology startups.
4. Filed international patent application (US2018/012836) for our ternary-based compounds.
5. Filed new provisional applications (US 62/634078 and US 62/693719) to cover our novel compositions that function from 10 K to 340 K.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. R. Ihnfeldt, R. Chen, E. Kim, X. Xu, and S. Jin, “Low Cost High Performance Magnetocaloric Materials for Hydrogen Liquefaction Applications.” Poster Presented at the 62nd Annual Conference on Magnetism and Magnetic Materials, Pittsburgh, PA, November 8, 2017.
2. R. Ihnfeldt, S. Jin, R. Chen, X. Xu, E. Caldwell, and E. Kim, “High Efficiency Magnetic Refrigeration Enabling Economic and SAFE Hydrogen Fuel.” Presented at the 2017 Cleantech Open Western Region Awards and Innovation Showcase, Fremont, CA, October 17, 2017.
3. R. Ihnfeldt, S. Jin, R. Chen, X. Xu, E. Caldwell, and E. Kim, “High Efficiency Magnetic Refrigeration Enabling Economic and SAFE Hydrogen Fuel.” Presented to the San Diego Regional Energy Innovation Network, San Diego, CA, November 14, 2017.
4. R. Ihnfeldt, S. Jin, R. Chen, X. Xu, E. Caldwell, and E. Kim, “High Efficiency Magnetic Refrigeration Enabling ZERO Emission Hydrogen Transportation.” Invited Presentation at Thermag VIII International Conference on Caloric Cooling, Darmstadt, Germany, September 19, 2018.
5. R. Ihnfeldt, S. Jin, R. Chen, X. Xu, E. Caldwell, and E. Kim, “High Performance Low Cost Magnetocaloric Materials,” Presented at Hydrogen Delivery Technical Team Review, Golden, CO, on February 28, 2018.

6. R. Ihnfeldt, S. Jin, R. Chen, X. Xu, E. Caldwell, and E. Kim, “Low-Cost Magnetocaloric Materials Discovery.” Poster Presentation at Fuel Cell Technologies Annual Merit Review, Washington, DC, on June 14, 2018.
7. E. Kim, X. Xu, R. Ihnfeldt, R. Chen, S. Jin, and C. Yoon, “The Mechanical Stability of La-Fe-Si Plate Over Magnetic Cycling.” Poster Presented at the 62nd Annual Conference on Magnetism and Magnetic Materials, Pittsburgh, PA, November 8, 2017.

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8. E. Kim, X. Xu, R. Ihnfeldt, R. Chen, S. Jin and C. Yoon, “The Mechanical Stability of La-Fe-Si Plate Over Magnetic Cycling,” Poster Presented at the 62nd Annual Conference on Magnetism and Magnetic Materials, Pittsburgh, PA, November 8, 2017.
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11. R. Ihnfeldt, S. Jin, R. Chen, X. Xu, E. Caldwell, and E. Kim, “Low-Cost Magnetocaloric Materials Discovery,” Poster Presentation at Fuel Cell Technologies Annual Merit Review, Washington, DC, June 14, 2018.