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(54) Title: MAGNETOCALORIC ALLOYS USEFUL FOR MAGNETIC REFRIGERATION APPLICATIONS

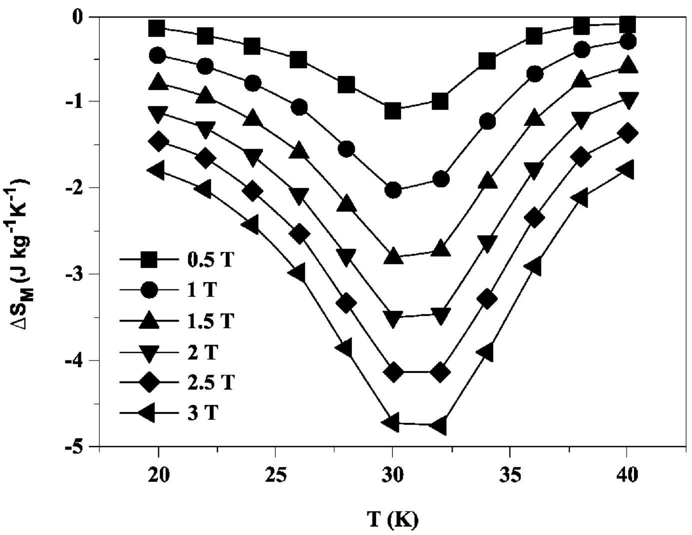

FIG. 1

(57) Abstract: Contemplated is a magnetocaloric materials comprising: $(Ce_xNd_{1-x})Si$ wherein x is in the range of about 0.1 to about 0.9, and wherein the magnetocaloric material exhibits a 2nd order magnetic phase transition in the temperature range of about 10 K to about 42 K. Also contemplated is a magnetocaloric material comprising: $RE(Si_yA_{1-y})$ wherein RE is selected from the group consisting of Ce, Nd, or Gd; wherein A is selected from the group consisting of Sn, Co. Al, Ni, Fe, Mn, Zn, or Cu: wherein y is in the range of about 0.1 to about 0.9. The alloys are fairly inexpensive, and in some cases exhibit only 2nd order magnetic phase transitions near their curie temperature, thus there are no thermal and structural hysteresis losses. This makes these compositions attractive candidates for use in magnetic refrigeration applications. The performance of the disclosed materials is similar or better to many of the known expensive rare-earth based magnetocaloric materials.

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MAGNETOCALORIC ALLOYS USEFUL FOR MAGNETIC REFRIGERATION APPLICATIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/443,955 filed on January 9, 2017 entitled "Magnetocaloric Alloys Useful for Magnetic Refrigeration Applications", and U.S. Provisional Patent Application No. 62/481,385 filed on April 4, 2017 entitled "Magnetocaloric Alloys Useful for Magnetic Refrigeration Applications", the contents of which are incorporated herein by reference in their entirety.

BACKGROUND

Field

[0002] Embodiments of the present invention generally relate to magnetocaloric materials comprising ternary alloys useful for magnetic refrigeration applications. In some embodiments, the disclosed alloys exhibit only 2^{nd} order magnetic phase transitions, with no thermal or structural hysteresis losses. This makes them attractive candidates for use in magnetic refrigeration applications. Additionally, the disclosed compositions are lower cost and higher performance than prior art materials.

Description of the Related Art

[0003] Magnetic Refrigeration utilizes the magnetocaloric effect (MCE), which is the temperature variation of a magnetic material after exposure to a magnetic field. A more detailed description of the magnetocaloric effect is described by Plaza and Campoy, *J. of Magnetism and Magnetic Mat.*, **321**, 446 (2009). A critical challenge of developing low cost magnetic refrigerators is the cost and availability of MCE materials, which are typically rare-earth and very expensive. The magnetocaloric effect (MCE) is an intrinsic property of a magnetic solid which has been successfully utilized for a variety of applications. 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. Thus, the materials considered for magnetic refrigeration devices must exhibit a magnetic phase transition temperature near the temperature region of interest, i.e. for hydrogen liquefaction ~20K, for nitrogen liquefaction ~80K, etc. Some of the most common MCE materials include RNi_2 (R=Gd, Dy and Ho) and RAl_2 (R=Er, Ho, Dy and $Dy_{0.5}Ho_{0.5}$, Dy_xEr_{1-x} and GdPd), all of which are rare-earth and expensive, according to B.G. Shen, J.R. Sun, F.X. Hu, H.W. Zhang, and Z.H. Cheng, *Adv. Mater.*, **21**, 4545 (2009). Kamiya et al., *Cryocoolers*, **14**, 637 (2007), successfully demonstrated a small scale hydrogen liquefaction magnetic refrigerator with efficiency approaching 90% of the Carnot efficiency, however, 280g of the rare-earth MCE material, dysprosium (bulk price ~$350/kg for 99% purity) gadolinium (bulk price ~$55/kg for 99.9% purity) aluminum garnet, was needed to achieve a maximum cooling power of 14.6W. These starting materials must further undergo significant processing to obtain the desired MCE properties which can increase the materials cost by 10-100X. Clearly, the capital cost of a magnetic refrigeration system capable of >400W of cooling power using the traditional rare-earth based MCE materials would far exceed its economic feasibility.

[0004] One of the major hurdles inhibiting the development of magnetic refrigeration technologies is the lack of commercially available low cost magnetocaloric materials that will actually function, for a long period of time, in a magnetic refrigeration environment such as the active magnetic regenerator (AMR) which is in development by several entities. While there has been extensive research discovering new materials with magnetocaloric properties, the majority of these material compositions will require substantial engineering to be compatible with AMR technologies. Materials such as GdSiGe or LaFeSi based alloys have sparked interest due to their giant magnetocaloric effect, however, this effect is due to a first order phase transition which has significant magnetic and thermal hysteresis and also exhibits structural changes, as described by Shen, J.R Sun, F.X. Hu, H.W. Zhang, and Z.H. Cheng, Adv. Mater., 21, 4545, 2009 and V. Provenzano, A.J. Shapiro, and R.D. Shull, Nature, 429, 853, 2004. The hysteresis reduces the reversibility of the MCE such that during high frequency magnetization and demagnetization, which is required for high efficiency AMRs, the magnitude of the MCE is drastically reduced. Methods to suppress thermal and magnetic hysteresis are possible, but require additional materials and processing and also act to suppress the MCE. Additionally, the structural changes typically manifest as volume expansion and contraction of the material, causing cracking during the magnetization and demagnetization cycles which quickly reduces the MCE response and lowers the thermal conductivity, making these materials incompatible in AMRs. While methods to improve mechanical stability of MCE materials with first order transitions can be employed, this will also require significant additional materials and processing which will increase cost. Further, scalable manufacturing of many MCE materials has yet to be demonstrated.

[0005] Literature has also suggested the microstructure of MCE materials can significantly influence its MCE properties. Micro- or nano- sized material synthesis occurs in either a top-down approach, which involves the breaking down of the bulk material into nano-sized structures or particles, or a bottom-up approach which refers to the building up of a material atom-by-atom, or molecule-by-molecule. Yang et al., *Journal of Alloys and Compounds*, **555**, 150 (2013), chemically synthesized (bottom-up approach) LaCaMnO nanoparticles and showed that variation in particle size shifted the MCE response temperature and also broadened the response temperature range compared to the bulk material. However, nanomaterial synthesis of the more common MCE alloys is extremely difficult. Using the top-down approach, surface oxidation which has minimal effect on bulk materials, is extremely rapid with the large surface area of nano-grains, and the MCE response of most alloys will be significantly reduced with even the slightest presence of oxygen. US Patent Application No. 2014/0290274 discloses LaFeSi based MCE materials with grain sizes of 15um-800um, where the micron sized grains were produced using ball milling techniques. The authors report an increase in magnetization response as the particle size decreases, with an optimal particle size in the range of 15um-200um. Particle sizes less than 10um showed drastically reduced MCE response which may be due to the surface oxidation of these smaller particles which is difficult to eliminate using traditional ball milling techniques. On the other hand, bottom-up approaches for metal alloys allow for enhanced control of particle size but are still under development, with oxidation, as well as obtaining the necessary crystalline structure presenting significant challenges.

SUMMARY

[0006] Some embodiments of the present invention provide a magnetocaloric material comprising $(Ce_xNd_{1-x})Si$ wherein x is in the range of about 0.1 to about 0.9. In some embodiments, the magnetocaloric material exhibits a 2^{nd} order magnetic phase transition in the temperature range of about 10K to about 42K. In some embodiments, the magnetocaloric material is $Ce_{0.1}Nd_{0.9}Si_{1.0}$, $Ce_{0.2}Nd_{0.8}Si_{1.0}$, $Ce_{0.3}Nd_{0.7}Si_{1.0}$, $Ce_{0.4}Nd_{0.6}Si_{1.0}$, $Ce_{0.5}Nd_{0.5}Si_{1.0}$, $Ce_{0.6}Nd_{0.4}Si_{1.0}$, $Ce_{0.7}Nd_{0.3}Si_{1.0}$, $Ce_{0.8}Nd_{0.2}Si_{1.0}$, $Ce_{0.9}Nd_{0.1}Si_{1.0}$, or any combination thereof.

[0007] Some embodiments of the present invention provide a magnetocaloric material comprising RE $(Si_y A_{1-y})$ wherein RE is selected from the group consisting of Ce, Nd, or Gd, and wherein A is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, Zn, or Cu, and wherein y is in the range of about 0.1 to about 0.9. In some embodiments the material is $Ce_{1.0}Si_{0.9}Sn_{0.1}$, $Ce_{1.0}Si_{0.8}Sn_{0.8}$, $Ce_{1.0}Si_{0.7}Sn_{0.3}$, $Ce_{1.0}Si_{0.6}Sn_{0.4}$, $Ce_{1.0}Si_{0.5}Sn_{0.5}$, $Ce_{1.0}Si_{0.4}Sn_{0.6}$, $Ce_{1.0}Si_{0.3}Sn_{0.7}$, $Ce_{1.0}Si_{0.2}Sn_{0.8}$, $Ce_{1.0}Si_{0.1}Sn_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Mn_{0.1}$, $Nd_{1.0}Si_{0.8}Mn_{0.8}$, $Nd_{1.0}Si_{0.7}Mn_{0.3}$, $Nd_{1.0}Si_{0.6}Mn_{0.4}$, $Nd_{1.0}Si_{0.5}Mn_{0.5}$, $Nd_{1.0}Si_{0.4}Mn_{0.6}$, $Nd_{1.0}Si_{0.3}Mn_{0.7}$, $Nd_{1.0}Si_{0.2}Mn_{0.8}$, $Nd_{1.0}Si_{0.1}Mn_{0.9}$, or any combination thereof. In some embodiments the material is $Gd_{1.0}Si_{0.9}Mn_{0.1}$, $Gd_{1.0}Si_{0.8}Mn_{0.8}$, $Gd_{1.0}Si_{0.7}Mn_{0.3}$, $Gd_{1.0}Si_{0.6}Mn_{0.4}$, $Gd_{1.0}Si_{0.5}Mn_{0.5}$, $Gd_{1.0}Si_{0.4}Mn_{0.6}$, $Gd_{1.0}Si_{0.3}Mn_{0.7}$, $Gd_{1.0}Si_{0.2}Mn_{0.8}$, $Gd_{1.0}Si_{0.1}Mn_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Fe_{0.1}$, $Nd_{1.0}Si_{0.8}Fe_{0.8}$, $Nd_{1.0}Si_{0.7}Fe_{0.3}$, $Nd_{1.0}Si_{0.6}Fe_{0.4}$, $Nd_{1.0}Si_{0.5}Fe_{0.5}$, $Nd_{1.0}Si_{0.4}Fe_{0.6}$, $Nd_{1.0}Si_{0.3}Fe_{0.7}$, $Nd_{1.0}Si_{0.2}Fe_{0.8}$, $Nd_{1.0}Si_{0.1}Fe_{0.9}$, or any combination thereof. In some embodiments the material is $Gd_{1.0}Si_{0.9}Fe_{0.1}$, $Gd_{1.0}Si_{0.8}Fe_{0.8}$, $Gd_{1.0}Si_{0.7}Fe_{0.3}$, $Gd_{1.0}Si_{0.6}Fe_{0.4}$, $Gd_{1.0}Si_{0.5}Fe_{0.5}$, $Gd_{1.0}Si_{0.4}Fe_{0.6}$, $Gd_{1.0}Si_{0.3}Fe_{0.7}$, $Gd_{1.0}Si_{0.2}Fe_{0.8}$, $Gd_{1.0}Si_{0.1}Fe_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Zn_{0.1}$, $Nd_{1.0}Si_{0.8}Zn_{0.8}$, $Nd_{1.0}Si_{0.7}Zn_{0.3}$, $Nd_{1.0}Si_{0.6}Zn_{0.4}$, $Nd_{1.0}Si_{0.5}Zn_{0.5}$, $Nd_{1.0}Si_{0.4}Zn_{0.6}$, $Nd_{1.0}Si_{0.3}Zn_{0.7}$, $Nd_{1.0}Si_{0.2}Zn_{0.8}$, $Nd_{1.0}Si_{0.1}Zn_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Ni_{0.1}$, $Nd_{1.0}Si_{0.8}Ni_{0.8}$, $Nd_{1.0}Si_{0.7}Ni_{0.3}$, $Nd_{1.0}Si_{0.6}Ni_{0.4}$, $Nd_{1.0}Si_{0.5}Ni_{0.5}$, $Nd_{1.0}Si_{0.4}Ni_{0.6}$, $Nd_{1.0}Si_{0.3}Ni_{0.7}$, $Nd_{1.0}Si_{0.2}Ni_{0.8}$, $Nd_{1.0}Si_{0.1}Ni_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Co_{0.1}$, $Nd_{1.0}Si_{0.8}Co_{0.8}$, $Nd_{1.0}Si_{0.7}Co_{0.3}$, $Nd_{1.0}Si_{0.6}Co_{0.4}$, $Nd_{1.0}Si_{0.5C}Co_{0.5}$, $Nd_{1.0}Si_{0.4}Co_{0.6}$, $Nd_{1.0}Si_{0.3}Co_{0.7}$, $Nd_{1.0}Si_{0.2}Co_{0.8}$, $Nd_{1.0}Si_{0.1}Co_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Cu_{0.1}$, $Nd_{1.0}Si_{0.8}Cu_{0.8}$, $Nd_{1.0}Si_{0.7}Cu_{0.3}$, $Nd_{1.0}Si_{0.6}Cu_{0.4}$, $Nd_{1.0}Si_{0.5C}Cu_{0.5}$, $Nd_{1.0}Si_{0.4}Cu_{0.6}$, $Nd_{1.0}Si_{0.3}Cu_{0.7}$, $Nd_{1.0}Si_{0.2}Cu_{0.8}$, $Nd_{1.0}Si_{0.1}Cu_{0.9}$, or any combination thereof.

[0008] In some embodiments, the magnetocaloric material comprises nano-grains, wherein at least one dimension of the nano-grains is in the range of about 0.1 nm to about 1000 nm. In some embodiments of the magnetocaloric material, the at least one dimension of the nanograins is in the range of about 1nm to about 100nm. In some embodiments of the magnetocaloric material, the at least one dimension of the nanograins is in the range of about 1nm to about 50nm.

[0009] Another embodiment of the invention is a magnetic refrigerator comprising the magnetocaloric material. In some embodiments, a magnetic refrigerator comprises a magnetocaloric material, wherein the magnetocaloric material comprises $(Ce_xNd_{1-x})Si$ wherein x is in the range of about 0.1 to about 0.9. In some embodiments, a magnetic refrigerator comprises a magnetocaloric material, wherein the magnetocaloric material comprises RE $(Si_y A_{1-y})$ wherein RE is selected from the group consisting of Ce, Nd, or Gd, and wherein A is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, or Cu, and wherein y is in the range of about 0.1 to about 0.9. In some embodiments, a magnetic refrigerator comprises a magnetocaloric material, wherein the magnetocaloric material comprises $Nd_{5.0}$ $(Si_z D_{3-z})$ wherein D is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, or Cu, and wherein z is in the range of about 0.1 to about 2.9.

[0010] Another embodiment of the invention is a method of manufacturing a heat pump, comprising fabricating at least one part of the heat pump from a magnetocaloric material. In some embodiments, a method of manufacturing a heat pump comprises fabricating at least one part of the heat pump from a magnetocaloric material, wherein the magnetocaloric material comprises $(Ce_xNd_{1-x})Si$ wherein x is in the range of about 0.1 to about 0.9. In some embodiments, a method of manufacturing a heat pump comprises fabricating at least one part of the heat pump from a magnetocaloric material, wherein the magnetocaloric material comprises RE $(Si_y A_{1-y})$ wherein RE is selected from the group consisting of Ce, Nd, or Gd, wherein A is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, or Cu, and wherein y is in the range of about 0.1 to about 0.9.

[0011] For purposes of summarizing aspects of the invention and the advantages achieved over the related art, certain objects and advantages of the invention are described in this disclosure. Of course, it is to be understood that not necessarily all such objects or advantages may be achieved in accordance with any particular embodiment of the invention. Thus, for example, those skilled in the art will recognize that the invention may be embodied or carried out in a manner that achieves or optimizes one advantage or group of advantages as taught herein without necessarily achieving other objects or advantages as may be taught or suggested herein.

Some embodiments relate to magnetocaloric materials comprising ternary alloys useful for magnetic refrigeration applications. The disclosed ternary alloys are Cerium, Neodymium, and/or Gadolinium based compositions that are fairly inexpensive, and in some cases exhibit only 2nd order magnetic phase transitions near their curie temperature, thus there are no thermal and structural hysteresis losses. This makes these compositions attractive candidates for use in magnetic refrigeration applications. Surprisingly, the performance of the disclosed materials is similar or better to many of the known expensive rare-earth based magnetocaloric materials.

[0012] Further aspects, features and advantages of this invention will become apparent from the detailed description of the embodiments which follow.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figure 1 illustrates the change in entropy versus temperature for a $Ce_{0.5}Nd_{0.5}Si$ alloy.

[0014] Figure 2 illustrates the magnetization versus temperature for several CeNdSi alloy's.

[0015] Figure 3 illustrates the magnetization versus temperature for a $Nd_{1.0}Si_{0.9}Zn_{0.1}$ alloy.

[0016] Figure 4 illustrates the magnetization versus temperature for a $Nd_{1.0}Si_{0.9}Ni_{0.1}$ alloy.

[0017] Figure 5 illustrates the magnetization versus temperature for a $Nd_{1.0}Si_{0.9}Mn_{0.1}$ alloy.

[0018] Figure 6 illustrates the magnetization versus temperature for a $Nd_{1.0}Si_{0.9}Fe_{0.1}$ alloy.

[0019] Figure 7 illustrates the magnetization versus temperature for a $Nd_{1.0}Si_{0.9}Al_{0.1}$ alloy.

[0020] Figure 8 illustrates the magnetization versus temperature for a $Nd_{1.0}Si_{0.9}Co_{0.1}$ alloy.

[0021] Figure 9 illustrates the magnetization versus temperature for a $Nd_{1.0}Si_{0.9}Cu_{0.1}$ alloy.

[0022] Figure 10 illustrates the magnetization versus temperature for a $Nd_{1.0}Si_{0.9}Sn_{0.1}$ alloy.

DETAILED DESCRIPTION

[0023] The magnetocaloric effect (MCE) is a phenomenon in which the temperature change of a suitable material is caused by exposing the material to a changing magnetic field. The magnetocaloric effect can be quantified with the equation below:

$$\Delta T_{ad} = -\int_{H_0}^{H_1} \left(\frac{T}{C(T,H)}\right)_H \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH$$

where T is the temperature, H is the applied magnetic field, C is the heat capacity of the working magnet (refrigerant) and M is the magnetization of the refrigerant. The temperature change in the material is caused by a change in the entropy of the material.

[0024] As used herein, the term “magnetocaloric effect” includes any phenomenon in which the temperature change of a material is caused by exposing the material to a changing magnetic field.

[0025] The magnetocaloric effect exhibited by most magnetocaloric materials is as follows: the temperature of the magnetocaloric material increases when the magnetic field is moved near or in contact with the magnetocaloric material, and wherein the temperature of the magnetocaloric material decreases when the magnetic field is moved away from the magnetocaloric material. Materials which undergo a magnetocaloric effect with application and removal of a magnetic field include, but are not limited to, Gadolinium based alloys. In some embodiments, the magnetocaloric material exhibits a magnetocaloric effect, wherein the temperature of the magnetocaloric material increases when the magnetic field is moved near or in contact with the magnetocaloric material, and wherein the temperature of the magnetocaloric material decreases when the magnetic field is moved away from the magnetocaloric material.

[0026] However, some magnetocaloric materials exhibit a inversed magnetocaloric effect, wherein the temperature of the magnetocaloric material decreases when the magnetic field is moved near or in contact with the magnetocaloric material, and wherein the temperature of the magnetocaloric material increases when the magnetic field is moved away from the magnetocaloric material. Materials which undergo an inverse magnetocaloric effect with application and removal of a magnetic field include, but are not limited to, Heusler alloys, which include, but are not limited to, NiMn based alloys. In some embodiments, the magnetocaloric material exhibits an inverse magnetocaloric effect, wherein the temperature of the magnetocaloric material decreases when the magnetic field is moved near or in contact with the magnetocaloric material, and wherein the temperature of the magnetocaloric material increases when the magnetic field is moved away from the magnetocaloric material.

[0027] Some embodiments of the present invention provide a magnetocaloric material comprising $(Ce_xNd_{1-x})Si$ wherein x is in the range of about 0.1 to about 0.9. In some embodiments, the magnetocaloric material exhibits a 2^{nd} order magnetic phase transition in the temperature range of about 10K to about 42K. In some embodiments, the magnetocaloric material is $Ce_{0.1}Nd_{0.9}Si_{1.0}$, $Ce_{0.2}Nd_{0.8}Si_{1.0}$, $Ce_{0.3}Nd_{0.7}Si_{1.0}$, $Ce_{0.4}Nd_{0.6}Si_{1.0}$, $Ce_{0.5}Nd_{0.5}Si_{1.0}$, $Ce_{0.6}Nd_{0.4}Si_{1.0}$, $Ce_{0.7}Nd_{0.3}Si_{1.0}$, $Ce_{0.8}Nd_{0.2}Si_{1.0}$, $Ce_{0.9}Nd_{0.1}Si_{1.0}$, or any combination thereof.

[0028] Some embodiments of the present invention provide a magnetocaloric material comprising RE $(Si_y A_{1-y})$ wherein RE is selected from the group consisting of Ce, Nd, or Gd, and wherein A is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, Zn, or Cu, and wherein y is in the range of about 0.1 to about 0.9. In some embodiments the material is $Ce_{1.0}Si_{0.9}Sn_{0.1}$, $Ce_{1.0}Si_{0.8}Sn_{0.8}$, $Ce_{1.0}Si_{0.7}Sn_{0.3}$, $Ce_{1.0}Si_{0.6}Sn_{0.4}$, $Ce_{1.0}Si_{0.5}Sn_{0.5}$, $Ce_{1.0}Si_{0.4}Sn_{0.6}$, $Ce_{1.0}Si_{0.3}Sn_{0.7}$, $Ce_{1.0}Si_{0.2}Sn_{0.8}$, $Ce_{1.0}Si_{0.1}Sn_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Mn_{0.1}$, $Nd_{1.0}Si_{0.8}Mn_{0.8}$, $Nd_{1.0}Si_{0.7}Mn_{0.3}$,

$Nd_{1.0}Si_{0.6}Mn_{0.4}$, $Nd_{1.0}Si_{0.5}Mn_{0.5}$, $Nd_{1.0}Si_{0.4}Mn_{0.6}$, $Nd_{1.0}Si_{0.3}Mn_{0.7}$, $Nd_{1.0}Si_{0.2}Mn_{0.8}$, $Nd_{1.0}Si_{0.1}Mn_{0.9}$, or any combination thereof. In some embodiments the material is $Gd_{1.0}Si_{0.9}Mn_{0.1}$, $Gd_{1.0}Si_{0.8}Mn_{0.8}$, $Gd_{1.0}Si_{0.7}Mn_{0.3}$, $Gd_{1.0}Si_{0.6}Mn_{0.4}$, $Gd_{1.0}Si_{0.5}Mn_{0.5}$, $Gd_{1.0}Si_{0.4}Mn_{0.6}$, $Gd_{1.0}Si_{0.3}Mn_{0.7}$, $Gd_{1.0}Si_{0.2}Mn_{0.8}$, $Gd_{1.0}Si_{0.1}Mn_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Fe_{0.1}$, $Nd_{1.0}Si_{0.8}Fe_{0.8}$, $Nd_{1.0}Si_{0.7}Fe_{0.3}$, $Nd_{1.0}Si_{0.6}Fe_{0.4}$, $Nd_{1.0}Si_{0.5}Fe_{0.5}$, $Nd_{1.0}Si_{0.4}Fe_{0.6}$, $Nd_{1.0}Si_{0.3}Fe_{0.7}$, $Nd_{1.0}Si_{0.2}Fe_{0.8}$, $Nd_{1.0}Si_{0.1}Fe_{0.9}$, or any combination thereof. In some embodiments the material is $Gd_{1.0}Si_{0.9}Fe_{0.1}$, $Gd_{1.0}Si_{0.8}Fe_{0.8}$, $Gd_{1.0}Si_{0.7}Fe_{0.3}$, $Gd_{1.0}Si_{0.6}Fe_{0.4}$, $Gd_{1.0}Si_{0.5}Fe_{0.5}$, $Gd_{1.0}Si_{0.4}Fe_{0.6}$, $Gd_{1.0}Si_{0.3}Fe_{0.7}$, $Gd_{1.0}Si_{0.2}Fe_{0.8}$, $Gd_{1.0}Si_{0.1}Fe_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Zn_{0.1}$, $Nd_{1.0}Si_{0.8}Zn_{0.8}$, $Nd_{1.0}Si_{0.7}Zn_{0.3}$, $Nd_{1.0}Si_{0.6}Zn_{0.4}$, $Nd_{1.0}Si_{0.5}Zn_{0.5}$, $Nd_{1.0}Si_{0.4}Zn_{0.6}$, $Nd_{1.0}Si_{0.3}Zn_{0.7}$, $Nd_{1.0}Si_{0.2}Zn_{0.8}$, $Nd_{1.0}Si_{0.1}Zn_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Ni_{0.1}$, $Nd_{1.0}Si_{0.8}Ni_{0.8}$, $Nd_{1.0}Si_{0.7}Ni_{0.3}$, $Nd_{1.0}Si_{0.6}Ni_{0.4}$, $Nd_{1.0}Si_{0.5}Ni_{0.5}$, $Nd_{1.0}Si_{0.4}Ni_{0.6}$, $Nd_{1.0}Si_{0.3}Ni_{0.7}$, $Nd_{1.0}Si_{0.2}Ni_{0.8}$, $Nd_{1.0}Si_{0.1}Ni_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Co_{0.1}$, $Nd_{1.0}Si_{0.8}Co_{0.8}$, $Nd_{1.0}Si_{0.7}Co_{0.3}$, $Nd_{1.0}Si_{0.6}Co_{0.4}$, $Nd_{1.0}Si_{0.5C}Co_{0.5}$, $Nd_{1.0}Si_{0.4}Co_{0.6}$, $Nd_{1.0}Si_{0.3}Co_{0.7}$, $Nd_{1.0}Si_{0.2}Co_{0.8}$, $Nd_{1.0}Si_{0.1}Co_{0.9}$, or any combination thereof. In some embodiments the material is $Nd_{1.0}Si_{0.9}Cu_{0.1}$, $Nd_{1.0}Si_{0.8}Cu_{0.8}$, $Nd_{1.0}Si_{0.7}Cu_{0.3}$, $Nd_{1.0}Si_{0.6}Cu_{0.4}$, $Nd_{1.0}Si_{0.5C}Cu_{0.5}$, $Nd_{1.0}Si_{0.4}Cu_{0.6}$, $Nd_{1.0}Si_{0.3}Cu_{0.7}$, $Nd_{1.0}Si_{0.2}Cu_{0.8}$, $Nd_{1.0}Si_{0.1}Cu_{0.9}$, or any combination thereof.

[0029] Some embodiments of the present invention provide a magnetocaloric material comprising (Ce_y Nd_{5-y}) $Si_{3.0}$ wherein y is in the range of about 0.1 to about 4.9. In some embodiments, the magnetocaloric material exhibits a magnetic phase transition in the temperature range of about 40K to about 300K. In some embodiments, the magnetocaloric material is $Ce_{0.1}Nd_{4.9}Si_{3.0}$, $Ce_{0.2}Nd_{4.8}Si_{3.0}$, $Ce_{0.3}Nd_{4.7}Si_{3.0}$, $Ce_{0.4}Nd_{4.6}Si_{3.0}$, $Ce_{0.5}Nd_{4.5}Si_{3.0}$, $Ce_{0.6}Nd_{4.4}Si_{3.0}$, $Ce_{0.7}Nd_{4.3}Si_{3.0}$, $Ce_{0.8}Nd_{4.2}Si_{3.0}$, $Ce_{0.9}Nd_{4.1}Si_{3.0}$, $Ce_{1.0}Nd_{4.0}Si_{3.0}$, $Ce_{1.1}Nd_{3.9}Si_{3.0}$, $Ce_{1.2}Nd_{3.8}Si_{3.0}$, $Ce_{1.3}Nd_{3.7}Si_{3.0}$, $Ce_{1.4}Nd_{3.6}Si_{3.0}$, $Ce_{1.5}Nd_{3.5}Si_{3.0}$, $Ce_{1.6}Nd_{3.4}Si_{3.0}$, $Ce_{1.7}Nd_{3.3}Si_{3.0}$, $Ce_{1.8}Nd_{3.2}Si_{3.0}$, $Ce_{1.9}Nd_{3.1}Si_{3.0}$, $Ce_{2.0}Nd_{3.0}Si_{3.0}$, $Ce_{2.1}Nd_{2.9}Si_{3.0}$, $Ce_{2.2}Nd_{2.8}Si_{3.0}$, $Ce_{2.3}Nd_{2.7}Si_{3.0}$, $Ce_{2.4}Nd_{2.6}Si_{3.0}$, $Ce_{2.5}Nd_{2.5}Si_{3.0}$, $Ce_{2.6}Nd_{2.4}Si_{3.0}$, $Ce_{2.7}Nd_{2.3}Si_{3.0}$, $Ce_{2.8}Nd_{2.2}Si_{3.0}$, $Ce_{2.9}Nd_{2.1}Si_{3.0}$, $Ce_{3.0}Nd_{2.0}Si_{3.0}$, $Ce_{3.1}Nd_{1.9}Si_{3.0}$, $Ce_{3.2}Nd_{1.8}Si_{3.0}$, $Ce_{3.3}Nd_{1.7}Si_{3.0}$, $Ce_{3.4}Nd_{1.6}Si_{3.0}$, $Ce_{3.5}Nd_{1.5}Si_{3.0}$, $Ce_{3.6}Nd_{1.4}Si_{3.0}$, $Ce_{3.7}Nd_{1.3}Si_{3.0}$, $Ce_{3.8}Nd_{1.2}Si_{3.0}$, $Ce_{3.9}Nd_{1.1}Si_{3.0}$, $Ce_{4.0}Nd_{1.0}Si_{3.0}$, $Ce_{4.1}Nd_{0.9}Si_{3.0}$,

$Ce_{4.2}Nd_{0.8}Si_{3.0}$, $Ce_{4.3}Nd_{0.7}Si_{3.0}$, $Ce_{4.4}Nd_{0.6}Si_{3.0}$, $Ce_{4.5}Nd_{0.5}Si_{3.0}$, $Ce_{4.6}Nd_{0.4}Si_{3.0}$, $Ce_{4.7}Nd_{0.3}Si_{3.0}$, $Ce_{4.8}Nd_{0.2}Si_{3.0}$, $Ce_{4.9}Nd_{0.1}Si_{3.0}$, or any combination thereof.

[0030] Some embodiments of the present invention provide a magnetocaloric material comprising Nd $(Si_y A_{1-y})$ wherein A is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, Zn, or Cu, and wherein y is in the range of about 0.1 to about 0.9. In some embodiments, the magnetocaloric material is $Nd_{1.0}Si_{0.9}Sn_{0.1}$, $Nd_{1.0}Si_{0.8}Sn_{0.8}$, $Nd_{1.0}Si_{0.7}Sn_{0.3}$, $Nd_{1.0}Si_{0.6}Sn_{0.4}$, $Nd_{1.0}Si_{0.5}Sn_{0.5}$, $Nd_{1.0}Si_{0.4}Sn_{0.6}$, $Nd_{1.0}Si_{0.3}Sn_{0.7}$, $Nd_{1.0}Si_{0.2}Sn_{0.8}$, $Nd_{1.0}Si_{0.1}Sn_{0.9}$, or any combination thereof. In some embodiments, the magnetocaloric material is $Nd_{1.0}Si_{0.9}Co_{0.1}$, $Nd_{1.0}Si_{0.8}Co_{0.8}$, $Nd_{1.0}Si_{0.7}Co_{0.3}$, $Nd_{1.0}Si_{0.6}Co_{0.4}$, $Nd_{1.0}Si_{0.5C}Co_{0.5}$, $Nd_{1.0}Si_{0.4}Co_{0.6}$, $Nd_{1.0}Si_{0.3}Co_{0.7}$, $Nd_{1.0}Si_{0.2}Co_{0.8}$, $Nd_{1.0}Si_{0.1}Co_{0.9}$, or any combination thereof. In some embodiments, the magnetocaloric material is $Nd_{1.0}Si_{0.9}Cu_{0.1}$, $Nd_{1.0}Si_{0.8}Cu_{0.8}$, $Nd_{1.0}Si_{0.7}Cu_{0.3}$, $Nd_{1.0}Si_{0.6}Cu_{0.4}$, $Nd_{1.0}Si_{0.5C}Cu_{0.5}$, $Nd_{1.0}Si_{0.4}Cu_{0.6}$, $Nd_{1.0}Si_{0.3}Cu_{0.7}$, $Nd_{1.0}Si_{0.2}Cu_{0.8}$, $Nd_{1.0}Si_{0.1}Cu_{0.9}$, or any combination thereof.

[0031] Some embodiments of the present invention provide a magnetocaloric material comprising $Nd_{5.0}$ $(Si_z D_{3-z})$ wherein D is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, Zn, or Cu, and wherein z is in the range of about 0.1 to about 2.9. In some embodiments, the magnetocaloric material exhibits a 2nd order magnetic phase transition in the temperature range of about 40K to about 300K. In some embodiments, the magnetocaloric material comprises $Nd_{5.0}$ $(Si_z Sn_{3-z})$ wherein z is in the range of about 0.1 to about 2.9. In some embodiments, the magnetocaloric material is $Nd_{5.0}Si_{0.1}Sn_{2.9}$, $Nd_{5.0}Si_{0.2}Sn_{2.8}$, $Nd_{5.0}Si_{0.3}Sn_{2.7}$, $Nd_{5.0}Si_{0.4}Sn_{2.6}$, $Nd_{5.0}Si_{0.5}Sn_{2.5}$, $Nd_{5.0}Si_{0.6}Sn_{2.4}$, $Nd_{5.0}Si_{0.7}Sn_{2.3}$, $Nd_{5.0}Si_{0.8}Sn_{2.2}$, $Nd_{5.0}Si_{0.9}Sn_{2.1}$, $Nd_{5.0}Si_{1.0}Sn_{2.0}$, $Nd_{5.0}Si_{1.1}Sn_{1.9}$, $Nd_{5.0}Si_{1.2}Sn_{1.8}$, $Nd_{5.0}Si_{1.3}Sn_{1.7}$, $Nd_{5.0}Si_{1.4}Sn_{1.6}$, $Nd_{5.0}Si_{1.5}Sn_{1.5}$, $Nd_{5.0}Si_{1.6}Sn_{1.4}$, $Nd_{5.0}Si_{1.7}Sn_{1.3}$, $Nd_{5.0}Si_{1.8}Sn_{1.2}$, $Nd_{5.0}Si_{1.9}Sn_{1.1}$, $Nd_{5.0}Si_{2.0}Sn_{1.0}$, $Nd_{5.0}Si_{2.1}Sn_{0.9}$, $Nd_{5.0}Si_{2.2}Sn_{0.8}$, $Nd_{5.0}Si_{2.3}Sn_{0.7}$, $Nd_{5.0}Si_{2.4}Sn_{0.6}$, $Nd_{5.0}Si_{2.5}Sn_{0.5}$, $Nd_{5.0}Si_{2.6}Sn_{0.4}$, $Nd_{5.0}Si_{2.7}Sn_{0.3}$, $Nd_{5.0}Si_{2.8}Sn_{0.2}$, $Nd_{5.0}Si_{2.9}Sn_{0.1}$, or any combination thereof.

[0032] In some embodiments, the magnetocaloric material comprises nano-grains, wherein at least one dimension of the nano-grains is in the range of about 0.1 nm to about 1000 nm. In some embodiments of the magnetocaloric material, the at least one dimension of the nanograins is in the range of about 1nm to about 100nm. In some embodiments of the magnetocaloric material, the at least one dimension of the nanograins is in the range of about 1nm to about 50nm.

[0033] Another embodiment of the invention is a magnetic refrigerator comprising the magnetocaloric material. In some embodiments, a magnetic refrigerator comprises a magnetocaloric material, wherein the magnetocaloric material comprises $(Ce_xNd_{1-x})Si$ wherein x is in the range of about 0.1 to about 0.9. In some embodiments, a magnetic refrigerator comprises a magnetocaloric material, wherein the magnetocaloric material comprises $(Ce_y\ Nd_{5-y})\ Si_{3.0}$ wherein y is in the range of about 0.1 to about 4.9. In some embodiments, a magnetic refrigerator comprises a magnetocaloric material, wherein the magnetocaloric material comprises $Nd\ (Si_y\ A_{1-y})$ wherein A is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, Zn, or Cu, and wherein x is in the range of about 0.1 to about 0.9. In some embodiments, a magnetic refrigerator comprises a magnetocaloric material, wherein the magnetocaloric material comprises $Nd_{5.0}\ (Si_z\ D_{3-z})$ wherein D is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, Zn or Cu, and wherein z is in the range of about 0.1 to about 2.9.

[0034] Another embodiment of the invention is a method of manufacturing a heat pump, comprising fabricating at least one part of the heat pump from a magnetocaloric material. In some embodiments, a method of manufacturing a heat pump comprises fabricating at least one part of the heat pump from a magnetocaloric material, wherein the magnetocaloric material comprises $(Ce_xNd_{1-x})Si$ wherein x is in the range of about 0.1 to about 0.9. In some embodiments, a method of manufacturing a heat pump comprises fabricating at least one part of the heat pump from a magnetocaloric material, wherein the magnetocaloric material comprises $(Ce_y\ Nd_{5-y})\ Si_{3.0}$ wherein y is in the range of about 0.1 to about 4.9. In some embodiments, a method of manufacturing a heat pump comprises fabricating at least one part of the heat pump from a magnetocaloric material, wherein the magnetocaloric material comprises $Nd\ (Si_y\ A_{1-y})$ wherein A is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, or Cu, and wherein x is in the range of about 0.1 to about 0.9. In some embodiments, a method of manufacturing a heat pump comprises fabricating at least one part of the heat pump from a magnetocaloric material, wherein the magnetocaloric material comprises $Nd_{5.0}\ (Si_z\ D_{3-z})$ wherein D is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, or Cu, and wherein z is in the range of about 0.1 to about 2.9.

[0035] In some embodiments, the nanograins of the magnetocaloric material are synthesized by methods known in the art, such as, but not limited to, spark erosion, ball milling, hydrothermal method, chemical precipitation synthesis, arc melting, chemical vapor deposition, physical vapor deposition, etc. In some embodiments, the nanograined manganese based magnetocaloric material is synthesized using a spark erosion technique.

[0036] In some embodiments, the nano-grained magnetocaloric material is formed into a pellet structure by various methods known in the art, such as sintering, hydraulic pressing, swaging, hot pressing, or any other method which effectively packs powder material into solid pellet form. In some embodiments, the magnetocaloric material may be formed into a porous structure.

[0037] R.D. McMichael, J.J. Ritter, and R.D. Shull, *J. Appl. Phys.*, **73**, (10) 6946 (1993), showed that the addition of iron nanoparticles to gadolinium-gallium composites increases the magnetocaloric response by a factor of 3-4, which may be due to a local field amplification effect. Therefore, incorporation of iron and/or its composites into the magnetocaloric material may act to locally amplify the magnetic field in the material, and further enhance the magnetocaloric response of the material. In some embodiments, the magnetocaloric material further comprises iron or any material, composite, or alloy comprising iron. In some embodiments the magnetocaloric material comprises nanoparticles of iron or nanoparticles of any material, composite, or alloy comprising iron. In some embodiments, the magnetocaloric pellets further comprise iron or any material, composite, or alloy comprising iron.

[0038] In some embodiments the magnetocaloric material comprises nanograins. In some embodiments, at least one dimension of the nanograins is in the range of about 0.1nm to about 1000nm. In some embodiments, at least one dimension of the nanograins is in the range of about 1nm to about 500nm. In some embodiments, at least one dimension of the nanograins is in the range of about 20nm to about 100nm. In some embodiments, at least one dimension of the nanograins is in the range of about 100nm to about 200nm. In some embodiments, at least one dimension of the nanograins is in the range of about 1nm to about

75nm. In some embodiments, at least one dimension of the nanograins is in the range of about 5nm to about 20nm. In some embodiments, at least one dimension of the nanograins is in the range of about 1nm to about 100nm. In some embodiments, the at least one dimension of the nanograins is in the range of about 1nm to about 50nm.

[0039] The response temperature of the magnetocaloric material may be adjusted with small changes in the composition of the material. In some embodiments, the response temperature of the magnetocaloric material is adjusted by changing the composition of the material. In some embodiments, the magnetocaloric material exhibits a magnetocaloric effect at any temperature in the range of about 1K to about 350K. In some embodiments, the magnetocaloric material exhibits a magnetocaloric effect at any temperature in the range of about 10K to about 50K. In some embodiments, the magnetocaloric material exhibits a magnetocaloric effect at any temperature in the range of about 50K to about 1000K. In some embodiments, the magnetocaloric material exhibits a magnetocaloric effect at any temperature in the range of about 100K to about 350K. In some embodiments, the magnetocaloric material exhibits a magnetocaloric effect at any temperature in the range of about 50K to about 200K. In some embodiments, the magnetocaloric nanomaterial exhibits a magnetocaloric effect at any temperature in the range of about 10K to about 80K.

[0040] For purposes of summarizing aspects of the invention and the advantages achieved over the related art, certain objects and advantages of the invention are described in this disclosure. Of course, it is to be understood that not necessarily all such objects or advantages may be achieved in accordance with any particular embodiment of the invention. Thus, for example, those skilled in the art will recognize that the invention may be embodied or carried out in a manner that achieves or optimizes one advantage or group of advantages as taught herein without necessarily achieving other objects or advantages as may be taught or suggested herein.

[0041] Further aspects, features and advantages of this invention will become apparent from the detailed example embodiments which follow.

EXAMPLES

[0042] The embodiments will be explained with respect to preferred embodiments which are not intended to limit the present invention. Further, in the present disclosure where conditions and/or structures are not specified, the skilled artisan in the art can readily provide such conditions and/or structures, in light of the teachings herein, as a matter of routine experimentation.

[0043] The object of this current invention is to provide magnetocaloric materials useful for magnetic refrigeration applications.

Example 1

[0044] A $Nd_{0.5}Ce_{0.5}Si_{1.0}$ ingot was prepared by arc melting in an argon atmosphere. The ingot was sealed in a quartz tube furnace under argon and annealed at 950C for 2 weeks. Figure 1 shows the DS vs entropy and Figure 2 shows the magnetization versus temperature for the $Nd_{0.5}Ce_{0.5}Si_{1.0}$ alloy with 2nd order phase transition occurring near 32K.

Example 2

[0045] A $Nd_{0.2}Ce_{0.8}Si_{1.0}$ ingot was prepared by arc melting in an argon atmosphere. The ingot was sealed in a quartz tube furnace under argon and annealed at 950C for 2 weeks. Figure 2 shows the magnetization versus temperature for the $Nd_{0.2}Ce_{0.8}Si_{1.0}$ alloy with 2nd order phase transition occurring near 15K.

Example 3

[0046] A $Nd_{0.4}Ce_{0.6}Si_{1.0}$ ingot was prepared by arc melting in an argon atmosphere. The ingot was sealed in a quartz tube furnace under argon and annealed at 950C for 2 weeks. Figure 2 shows the magnetization versus temperature for the $Nd_{0.4}Ce_{0.6}Si_{1.0}$ alloy with 2nd order phase transition occurring near 25K.

Example 4

[0047] A $Nd_{0.6}Ce_{0.4}Si_{1.0}$ ingot was prepared by arc melting in an argon atmosphere. The ingot was sealed in a quartz tube furnace under argon and annealed at 950C for 2 weeks. Figure 2 shows the magnetization versus temperature for the $Nd_{0.6}Ce_{0.4}Si_{1.0}$ alloy with 2nd order phase transition occurring near 36K.

Example 5

[0048] A $Nd_{0.8}Ce_{0.2}Si_{1.0}$ ingot was prepared by arc melting in an argon atmosphere. The ingot was sealed in a quartz tube furnace under argon and annealed at 950C for 2 weeks. Figure 2 shows the magnetization versus temperature for the $Nd_{0.8}Ce_{0.2}Si_{1.0}$ alloy with 2^{nd} order phase transition occurring near 42K.

Example 6

[0049] A $Nd_{1.0}Si_{0.9}Zn_{0.1}$ ingot was prepared by arc melting in an argon atmosphere. Figure 3 shows the magnetization versus temperature for the $Nd_{1.0}Si_{0.9}Zn_{0.1}$ alloy with 2^{nd} order phase transition occurring near 75K.

Example 6

[0050] A $Nd_{1.0}Si_{0.9}Ni_{0.1}$ ingot was prepared by arc melting in an argon atmosphere. Figure 4 shows the magnetization versus temperature for the $Nd_{1.0}Si_{0.9}Ni_{0.1}$ alloy with 2^{nd} order phase transition occurring near 75K.

Example 7

[0051] A $Nd_{1.0}Si_{0.9}Mn_{0.1}$ ingot was prepared by arc melting in an argon atmosphere. Figure 5 shows the magnetization versus temperature for the $Nd_{1.0}Si_{0.9}Mn_{0.1}$ alloy with 2^{nd} order phase transition occurring near 125K.

Example 8

[0052] A $Nd_{1.0}Si_{0.9}Fe_{0.1}$ ingot was prepared by arc melting in an argon atmosphere. Figure 6 shows the magnetization versus temperature for the $Nd_{1.0}Si_{0.9}Fe_{0.1}$ alloy with 2^{nd} order phase transition occurring near 75K.

Example 9

[0053] A $Nd_{1.0}Si_{0.9}Al_{0.1}$ ingot was prepared by arc melting in an argon atmosphere. Figure 7 shows the magnetization versus temperature for the $Nd_{1.0}Si_{0.9}Al_{0.1}$ alloy with 2^{nd} order phase transition occurring less than 50K.

Example 10

[0054] A $Nd_{1.0}Si_{0.9}Co_{0.1}$ ingot was prepared by arc melting in an argon atmosphere. Figure 8 shows the magnetization versus temperature for the $Nd_{1.0}Si_{0.9}Co_{0.1}$ alloy with 2^{nd} order phase transition occurring near 75K.

Example 11

[0055] A $Nd_{1.0}Si_{0.9}Cu_{0.1}$ ingot was prepared by arc melting in an argon atmosphere. Figure 9 shows the magnetization versus temperature for the $Nd_{1.0}Si_{0.9}Cu_{0.1}$ alloy with 2^{nd} order phase transition occurring near 75K.

Example 12

[0056] A $Nd_{1.0}Si_{0.9}Sn_{0.1}$ ingot was prepared by arc melting in an argon atmosphere. Figure 10 shows the magnetization versus temperature for the $Nd_{1.0}Si_{0.9}Sn_{0.1}$ alloy with 2^{nd} order phase transition occurring less than 50K.

Example 13

[0057] An example magnetic refrigerator comprising the disclosed magnetocaloric material is made by the following steps 1) preparing the magnetocaloric material into thin plates or millimeter sized spherical balls, 2) placing the magnetocaloric material into a magnetic field, where the application of the magnetic field causes the material to heat up, 3) using a heat transfer fluid to remove the heat from the magnetocaloric material, 4) then removing the magnetic field causing the magnetocaloric material to cool down, 5) then exposing the cold magnetocaloric material to the desired refrigeration environment where heat from the refrigeration environment is transferred to the magnetocaloric material, 6) then repeating steps 1 to 5 to create a refrigeration cycle which maintains a desired cold temperature within the refrigeration environment.

Example 14

[0058] An example magnetic refrigerator comprising the disclosed magnetocaloric material is made by the following similar steps as in Example 13, except that a heat transfer fluid is used in step 5 to expose the cold magnetocaloric material to the desired refrigeration environment, where the heat from the refrigeration environment is transferred to the heat transfer fluid.

Example 15

[0059] An example heat pump comprising fabricating at least one part of the heat pump from a magnetocaloric material is made by incorporating at least one magnetocaloric material of the disclosed invention, at least one permanent magnet, and at least one mechanical movement system; wherein the magnetic field generated by the permanent magnet enables the magnetocaloric effect of the magnetocaloric material when at least one oscillation cycle is performed by the mechanical movement system, wherein a change in temperature of the magnetocaloric material occurs when the magnetocaloric material is moved into or out of a magnetic field; and wherein the mechanical movement system performs the at least one oscillation cycle by physically moving the permanent magnet, the magnetocaloric material, a magnet shielding material, or any combination thereof; and wherein the at least one oscillation cycle comprises exposing the magnetic field to the magnetocaloric material at a predefined magnetic field ramp-up speed, holding the magnetic field near or in contact with the magnetocaloric material for a specified contact holding time, removing the magnetic field from the magnetocaloric material at a predefined ramp-down speed, and holding the magnetic field away from the magnetocaloric material for a specified removed holding time; and wherein the at least one oscillation cycle is optimized to provide cooling on one side of the heat pump device.

[0060] For purposes of summarizing aspects of the invention and the advantages achieved over the related art, certain objects and advantages of the invention are described in this disclosure. Of course, it is to be understood that not necessarily all such objects or advantages may be achieved in accordance with any particular embodiment of the invention. Thus, for example, those skilled in the art will recognize that the invention may be embodied or carried out in a manner that achieves or optimizes one advantage or group of advantages as taught herein without necessarily achieving other objects or advantages as may be taught or suggested herein. It will be understood by those of skill in the art that numerous and various modifications can be made without departing from the spirit of the present invention. Therefore, it should be clearly understood that the forms of the present invention are illustrative only and are not intended to limit the scope of the present invention.

WHAT IS CLAIMED IS:

1. A magnetocaloric material comprising:

$(Ce_x Nd_{1-x}) Si$

wherein x is in the range of about 0.1 to about 0.9,

and wherein the magnetocaloric material exhibits a 2nd order magnetic phase transition in the temperature range of about 10K to about 42K.

2. The magnetocaloric material of claim 2, wherein the material is $Ce_{0.1}Nd_{0.9}Si_{1.0}$, $Ce_{0.2}Nd_{0.8}Si_{1.0}$, $Ce_{0.3}Nd_{0.7}Si_{1.0}$, $Ce_{0.4}Nd_{0.6}Si_{1.0}$, $Ce_{0.5}Nd_{0.5}Si_{1.0}$, $Ce_{0.6}Nd_{0.4}Si_{1.0}$, $Ce_{0.7}Nd_{0.3}Si_{1.0}$, $Ce_{0.8}Nd_{0.2}Si_{1.0}$, $Ce_{0.9}Nd_{0.1}Si_{1.0}$, or any combination thereof.

3. A magnetocaloric material comprising:

$RE (Si_y A_{1-y})$

wherein RE is selected from the group consisting of Ce, Nd, or Gd;

wherein A is selected from the group consisting of Sn, Co, Al, Ni, Fe, Mn, Zn, or Cu;

wherein y is in the range of about 0.1 to about 0.9.

4. The magnetocaloric material of claim 3, wherein the material is $Ce_{1.0}Si_{0.9}Sn_{0.1}$, $Ce_{1.0}Si_{0.8}Sn_{0.8}$, $Ce_{1.0}Si_{0.7}Sn_{0.3}$, $Ce_{1.0}Si_{0.6}Sn_{0.4}$, $Ce_{1.0}Si_{0.5}Sn_{0.5}$, $Ce_{1.0}Si_{0.4}Sn_{0.6}$, $Ce_{1.0}Si_{0.3}Sn_{0.7}$, $Ce_{1.0}Si_{0.2}Sn_{0.8}$, $Ce_{1.0}Si_{0.1}Sn_{0.9}$, or any combination thereof.

5. The magnetocaloric material of claim 3, wherein the material is $Nd_{1.0}Si_{0.9}Mn_{0.1}$, $Nd_{1.0}Si_{0.8}Mn_{0.8}$, $Nd_{1.0}Si_{0.7}Mn_{0.3}$, $Nd_{1.0}Si_{0.6}Mn_{0.4}$, $Nd_{1.0}Si_{0.5}Mn_{0.5}$, $Nd_{1.0}Si_{0.4}Mn_{0.6}$, $Nd_{1.0}Si_{0.3}Mn_{0.7}$, $Nd_{1.0}Si_{0.2}Mn_{0.8}$, $Nd_{1.0}Si_{0.1}Mn_{0.9}$, or any combination thereof.

6. The magnetocaloric material of claim 5, wherein the material is $Gd_{1.0}Si_{0.9}Mn_{0.1}$, $Gd_{1.0}Si_{0.8}Mn_{0.8}$, $Gd_{1.0}Si_{0.7}Mn_{0.3}$, $Gd_{1.0}Si_{0.6}Mn_{0.4}$, $Gd_{1.0}Si_{0.5}Mn_{0.5}$, $Gd_{1.0}Si_{0.4}Mn_{0.6}$, $Gd_{1.0}Si_{0.3}Mn_{0.7}$, $Gd_{1.0}Si_{0.2}Mn_{0.8}$, $Gd_{1.0}Si_{0.1}Mn_{0.9}$, or any combination thereof.

7. The magnetocaloric material of claim 3, wherein the material is $Nd_{1.0}Si_{0.9}Fe_{0.1}$, $Nd_{1.0}Si_{0.8}Fe_{0.8}$, $Nd_{1.0}Si_{0.7}Fe_{0.3}$, $Nd_{1.0}Si_{0.6}Fe_{0.4}$, $Nd_{1.0}Si_{0.5}Fe_{0.5}$, $Nd_{1.0}Si_{0.4}Fe_{0.6}$, $Nd_{1.0}Si_{0.3}Fe_{0.7}$, $Nd_{1.0}Si_{0.2}Fe_{0.8}$, $Nd_{1.0}Si_{0.1}Fe_{0.9}$, or any combination thereof.

8. The magnetocaloric material of claim 3, wherein the material is $Gd_{1.0}Si_{0.9}Fe_{0.1}$, $Gd_{1.0}Si_{0.8}Fe_{0.8}$, $Gd_{1.0}Si_{0.7}Fe_{0.3}$, $Gd_{1.0}Si_{0.6}Fe_{0.4}$, $Gd_{1.0}Si_{0.5}Fe_{0.5}$, $Gd_{1.0}Si_{0.4}Fe_{0.6}$, $Gd_{1.0}Si_{0.3}Fe_{0.7}$, $Gd_{1.0}Si_{0.2}Fe_{0.8}$, $Gd_{1.0}Si_{0.1}Fe_{0.9}$, or any combination thereof.

9. The magnetocaloric material of claim 3, wherein the material is $Nd_{1.0}Si_{0.9}Zn_{0.1}$, $Nd_{1.0}Si_{0.8}Zn_{0.8}$, $Nd_{1.0}Si_{0.7}Zn_{0.3}$, $Nd_{1.0}Si_{0.6}Zn_{0.4}$, $Nd_{1.0}Si_{0.5}Zn_{0.5}$, $Nd_{1.0}Si_{0.4}Zn_{0.6}$, $Nd_{1.0}Si_{0.3}Zn_{0.7}$, $Nd_{1.0}Si_{0.2}Zn_{0.8}$, $Nd_{1.0}Si_{0.1}Zn_{0.9}$, or any combination thereof.

10. The magnetocaloric material of claim 3, wherein the material is $Nd_{1.0}Si_{0.9}Ni_{0.1}$, $Nd_{1.0}Si_{0.8}Ni_{0.8}$, $Nd_{1.0}Si_{0.7}Ni_{0.3}$, $Nd_{1.0}Si_{0.6}Ni_{0.4}$, $Nd_{1.0}Si_{0.5}Ni_{0.5}$, $Nd_{1.0}Si_{0.4}Ni_{0.6}$, $Nd_{1.0}Si_{0.3}Ni_{0.7}$, $Nd_{1.0}Si_{0.2}Ni_{0.8}$, $Nd_{1.0}Si_{0.1}Ni_{0.9}$, or any combination thereof.

11. The magnetocaloric material of claim 3, wherein the material is $Nd_{1.0}Si_{0.9}Co_{0.1}$, $Nd_{1.0}Si_{0.8}Co_{0.8}$, $Nd_{1.0}Si_{0.7}Co_{0.3}$, $Nd_{1.0}Si_{0.6}Co_{0.4}$, $Nd_{1.0}Si_{0.5C}Co_{0.5}$, $Nd_{1.0}Si_{0.4}Co_{0.6}$, $Nd_{1.0}Si_{0.3}Co_{0.7}$, $Nd_{1.0}Si_{0.2}Co_{0.8}$, $Nd_{1.0}Si_{0.1}Co_{0.9}$, or any combination thereof.

12. The magnetocaloric material of claim 3, wherein the material is $Nd_{1.0}Si_{0.9}Cu_{0.1}$, $Nd_{1.0}Si_{0.8}Cu_{0.8}$, $Nd_{1.0}Si_{0.7}Cu_{0.3}$, $Nd_{1.0}Si_{0.6}Cu_{0.4}$, $Nd_{1.0}Si_{0.5C}Cu_{0.5}$, $Nd_{1.0}Si_{0.4}Cu_{0.6}$, $Nd_{1.0}Si_{0.3}Cu_{0.7}$, $Nd_{1.0}Si_{0.2}Cu_{0.8}$, $Nd_{1.0}Si_{0.1}Cu_{0.9}$, or any combination thereof.

13. The magnetocaloric material of any of claims 1 to 9, wherein the material comprises nano-grains, wherein at least one dimension of the nano-grains is in the range of about 0.1 nm to about 1000 nm.

14. The magnetocaloric material of claim 10, wherein the at least one dimension of the nanograins is in the range of about 1nm to about 100nm.

15. The magnetocaloric material of claim 11, wherein the at least one dimension of the nanograins is in the range of about 1nm to about 50nm.

16. A magnetic refrigerator, comprising the magnetocaloric material of any of claims 1 to 12.

17. A method of manufacturing a heat pump, comprising fabricating at least one part of the heat pump from the material of any of claims 1 to 12.

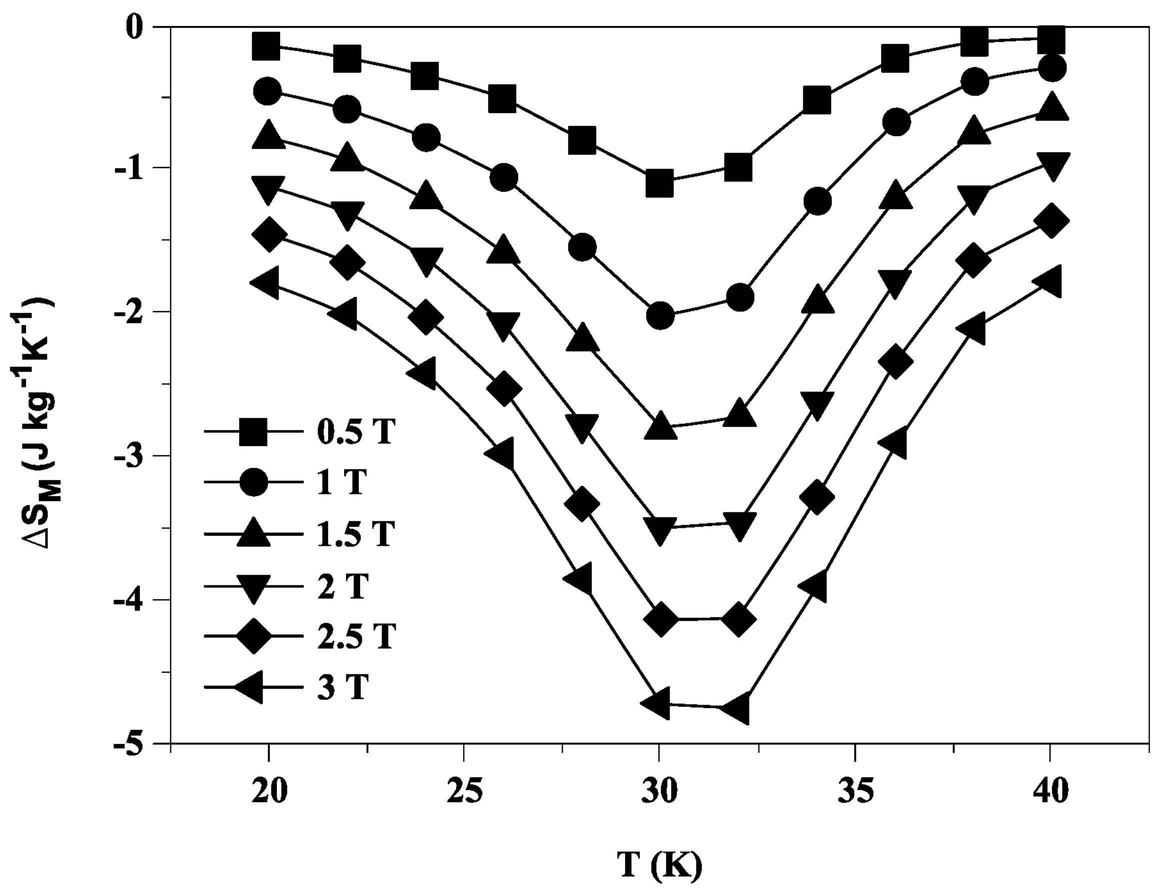


FIG. 1

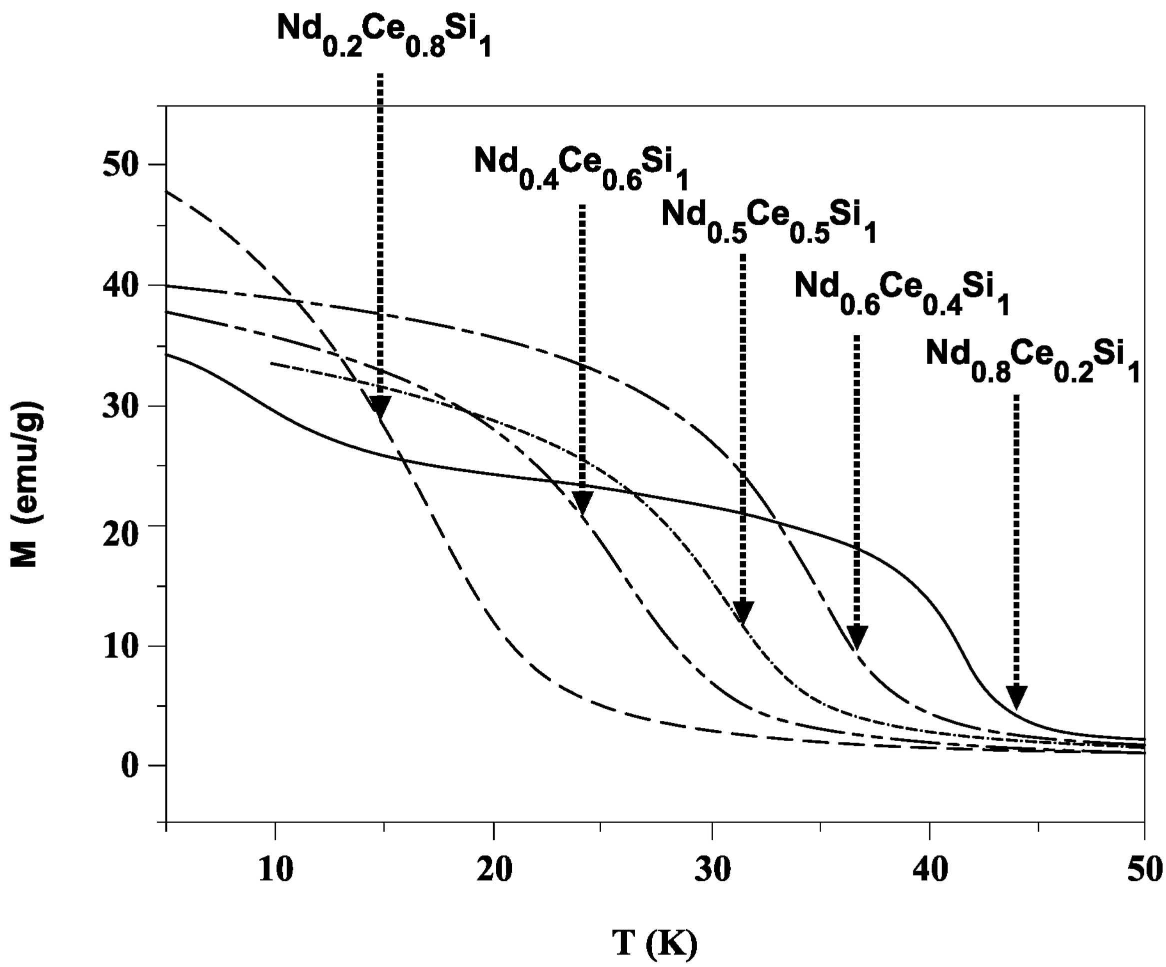

Nd0.2Ce0.8Si1
Nd0.4Ce0.6Si1
Nd0.5Ce0.5Si1
Nd0.6Ce0.4Si1
Nd0.8Ce0.2Si1
M (emu/g)
T (K)
0
10
20
30
40
50

FIG.2

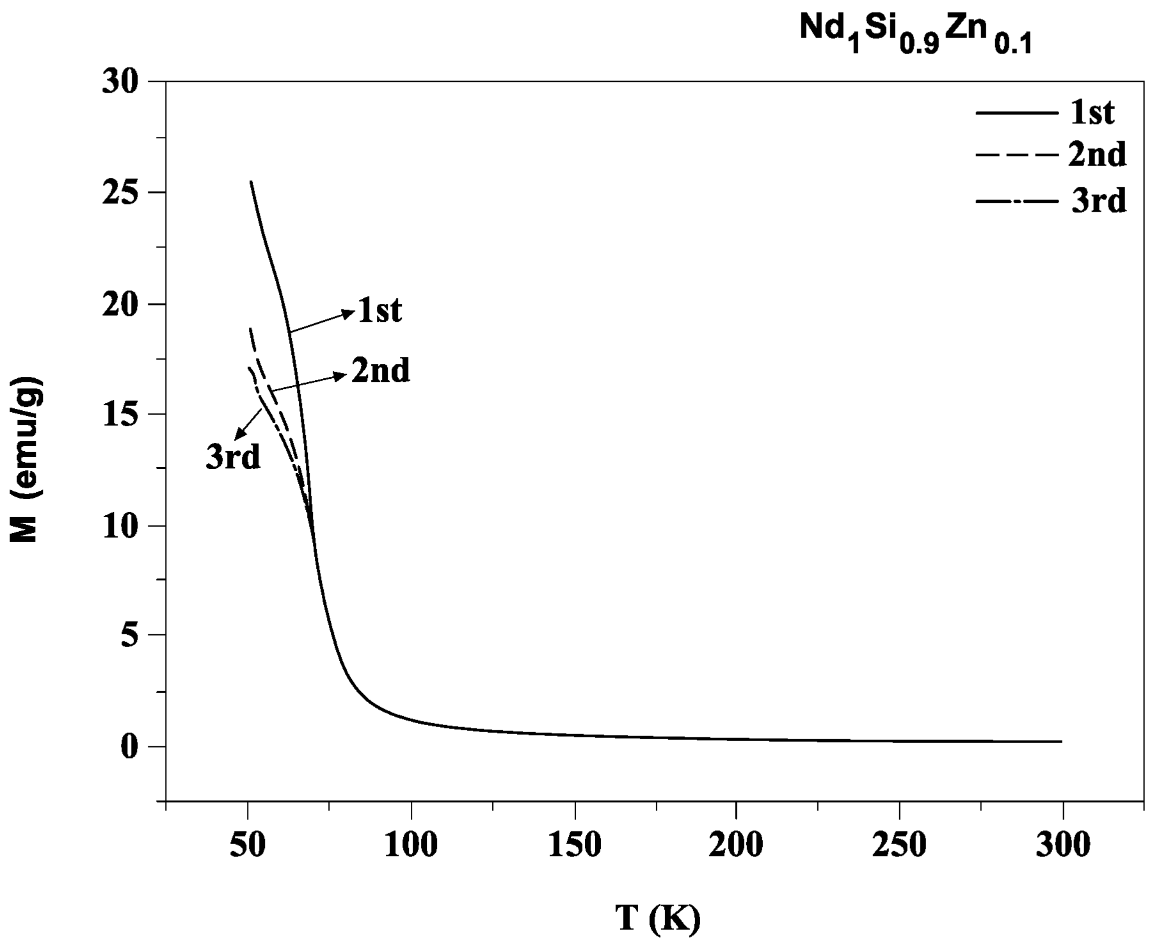

Nd1Si0.9Zn0.1
1st
2nd
3rd
1st
2nd
3rd
M (emu/g)
0
5
10
15
20
25
30
50
100
150
200
250
300
T (K)

FIG. 3

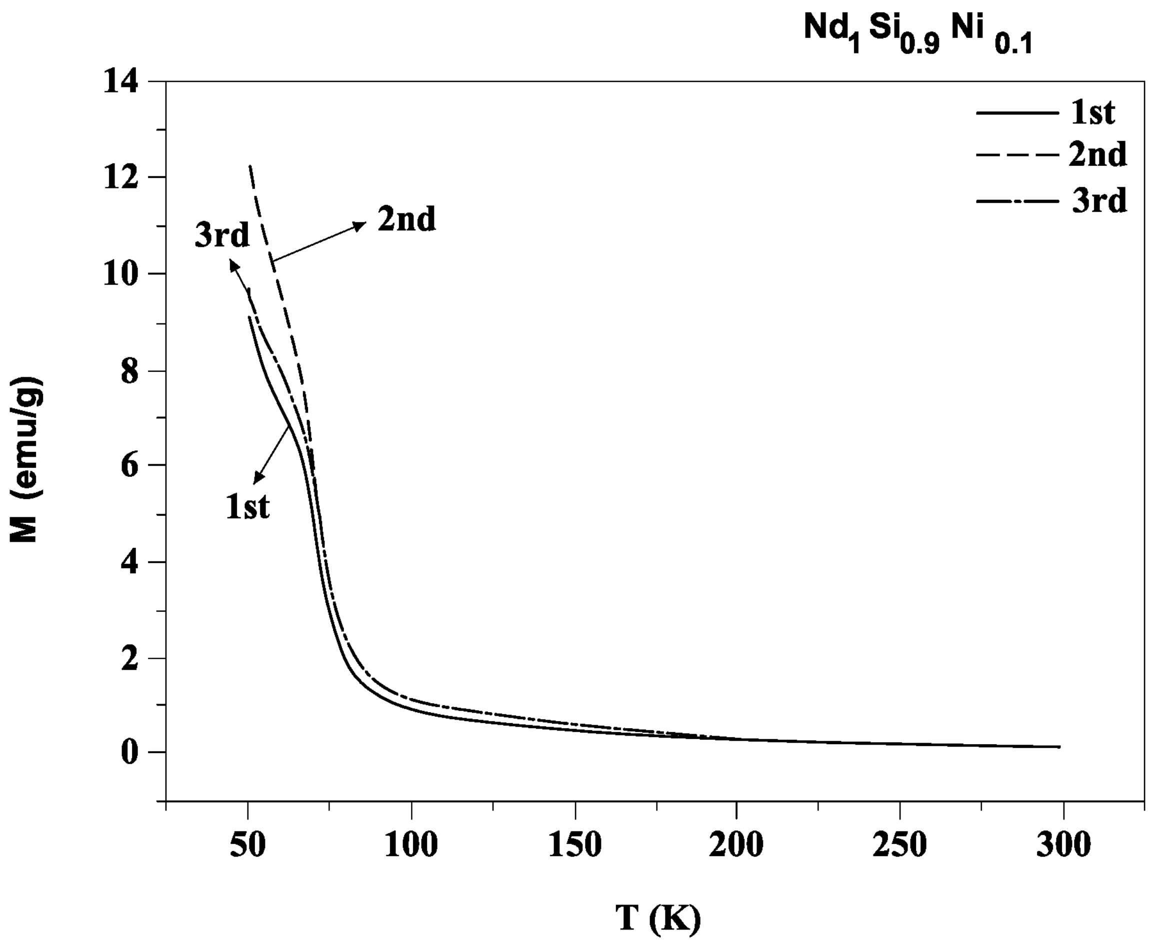

Nd1 Si0.9 Ni 0.1
14
12
10
8
6
4
2
0
M (emu/g)
50
100
150
200
250
300
T (K)
1st
2nd
3rd
3rd
2nd
1st

FIG. 4

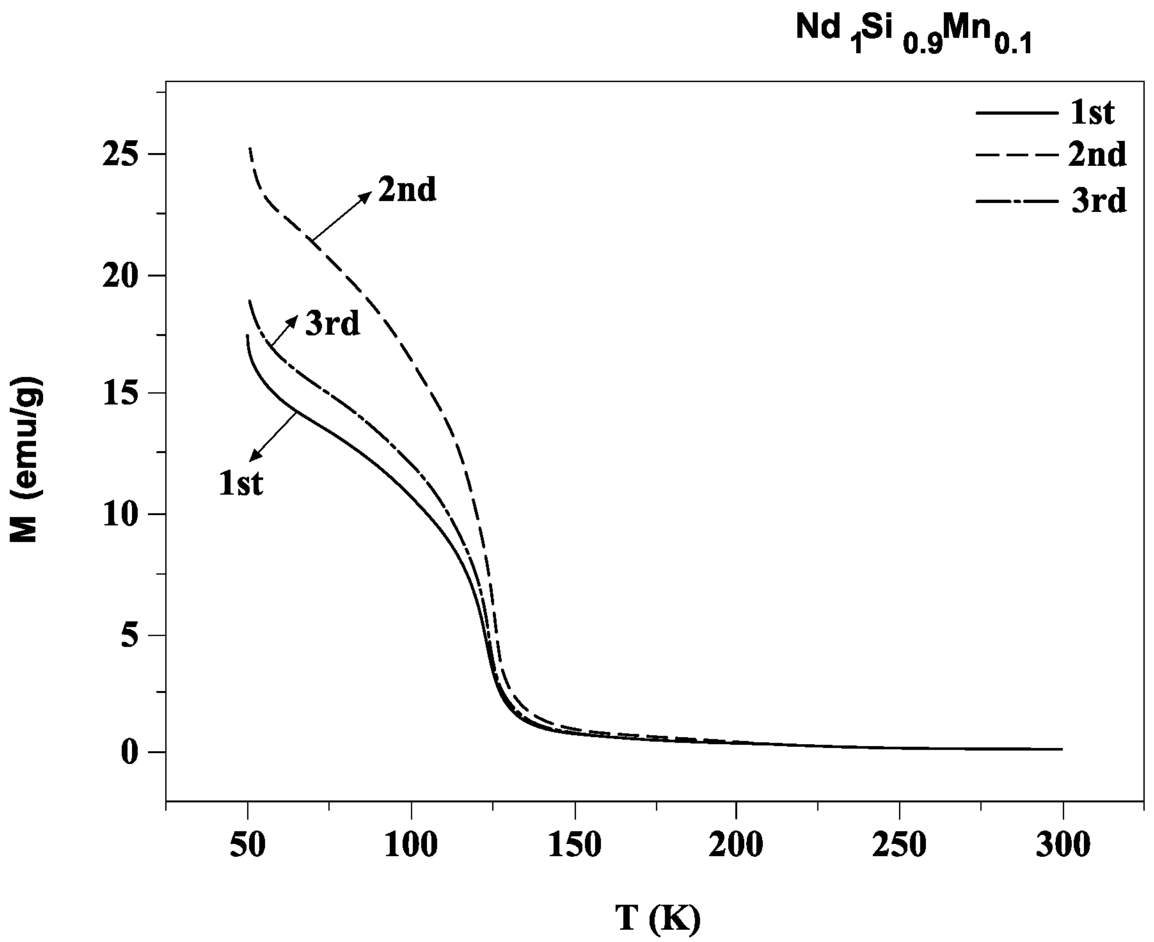

Nd 1Si 0.9Mn0.1
1st
2nd
3rd
2nd
3rd
1st
25
20
15
10
5
0
M (emu/g)
50
100
150
200
250
300
T (K)

FIG. 5

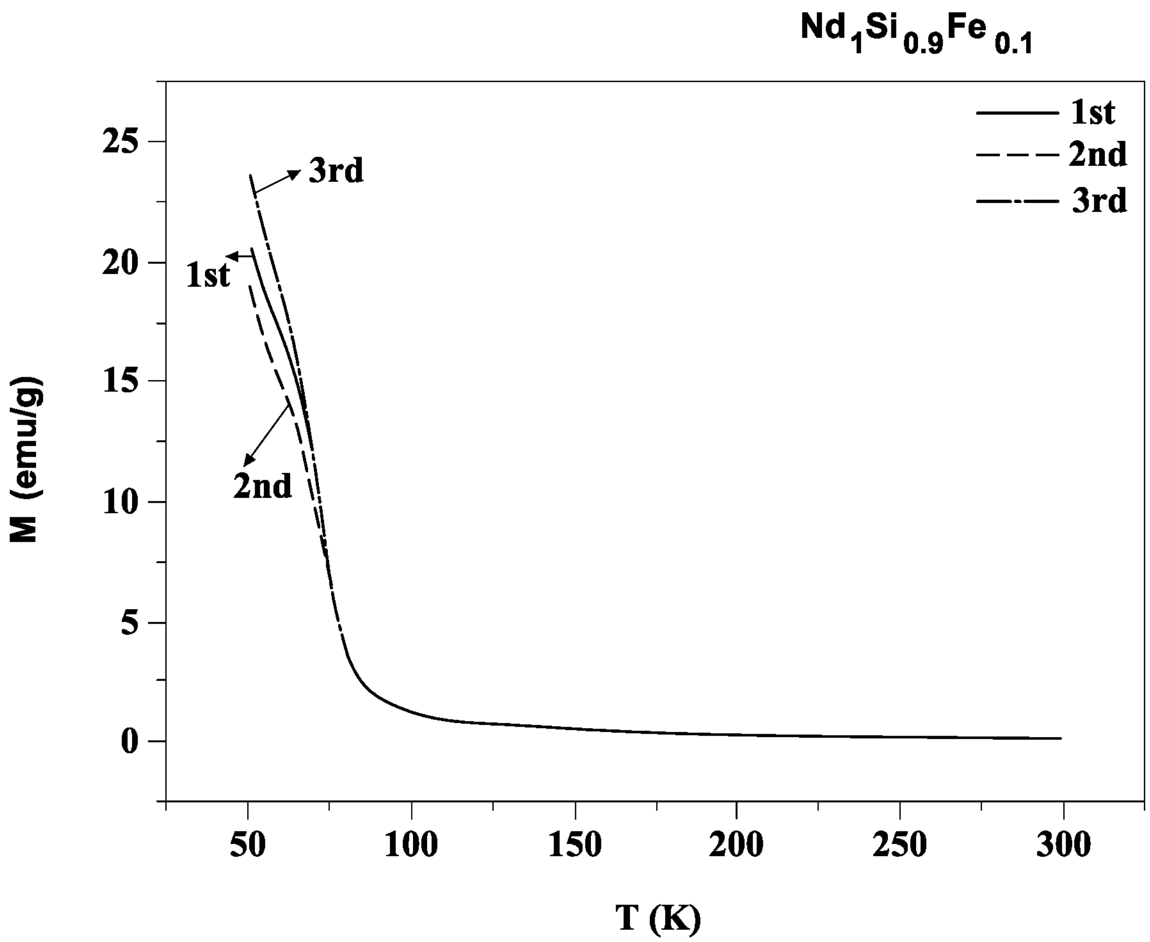

$Nd_1Si_{0.9}Fe_{0.1}$
1st
2nd
3rd
3rd
1st
2nd
25
20
15
10
5
0
M (emu/g)
50
100
150
200
250
300
T (K)

FIG. 6

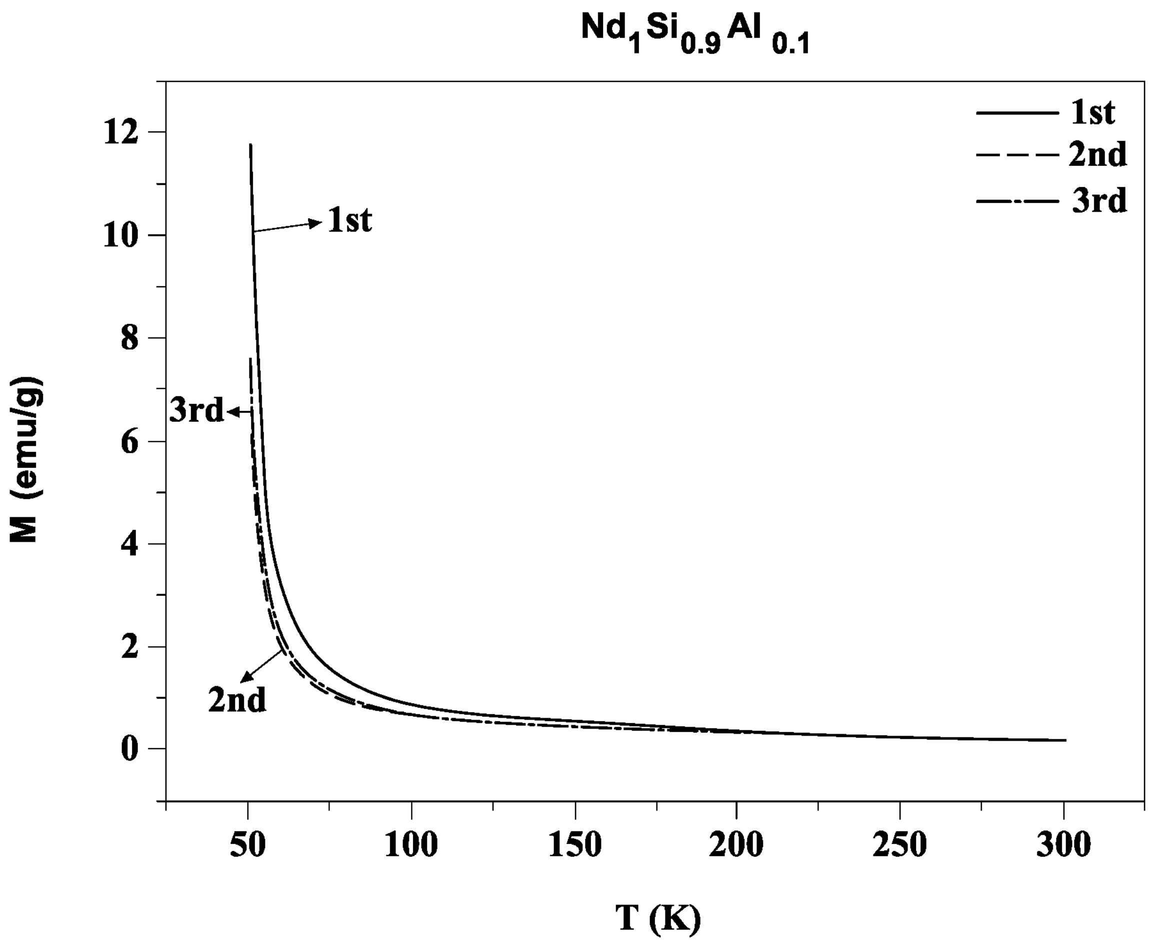
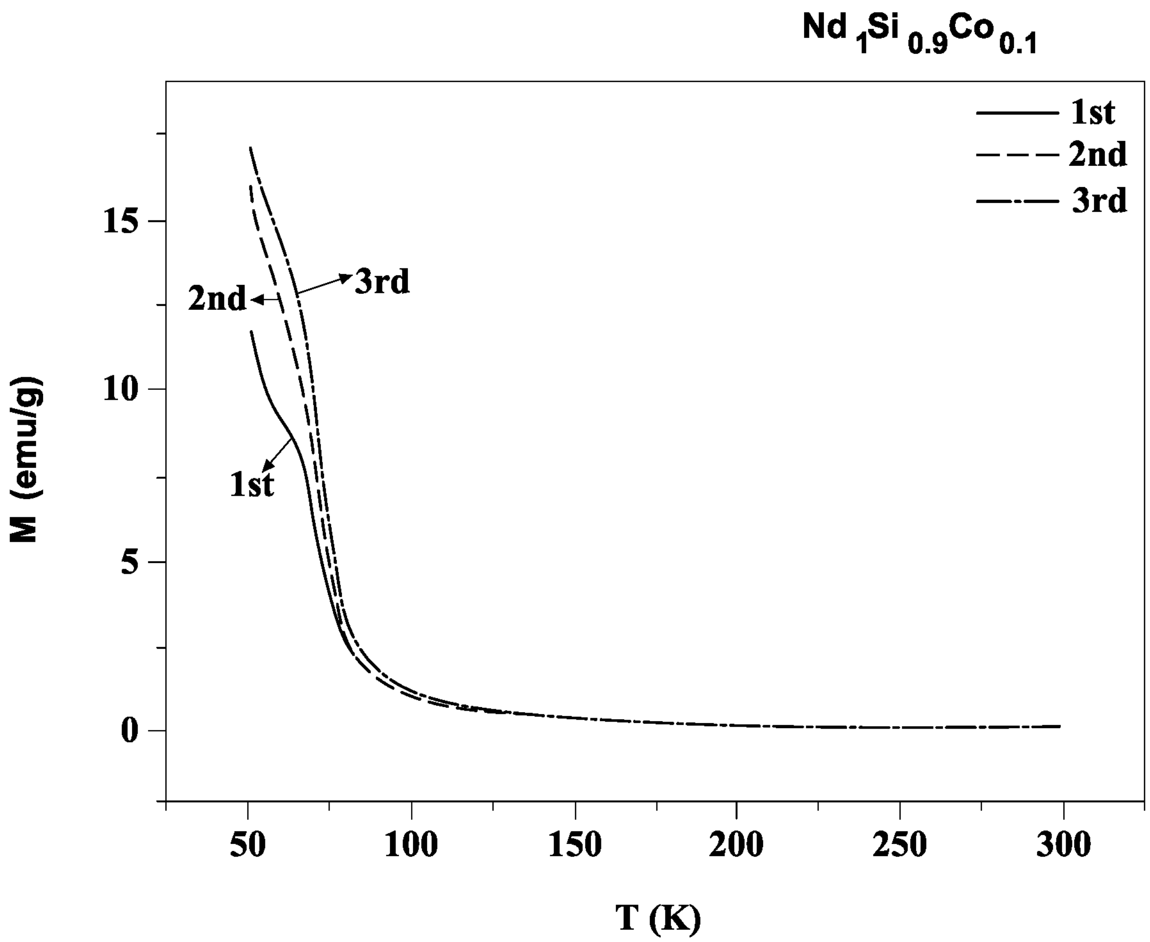
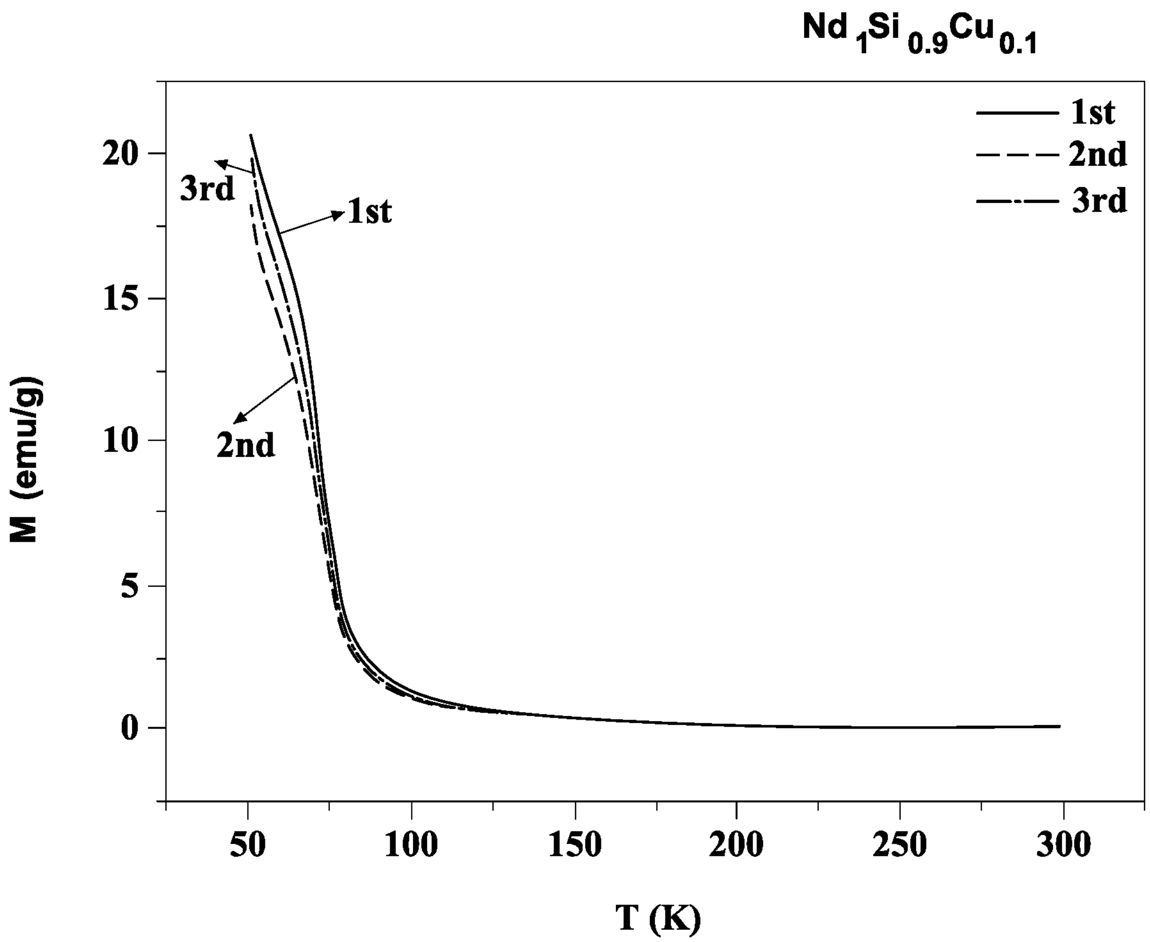

$Nd_1Si_{0.9}Al_{0.1}$
1st
2nd
3rd
1st
3rd
2nd
12
10
8
6
4
2
0
M (emu/g)
50
100
150
200
250
300
T (K)

FIG. 7



$Nd_1Si_{0.9}Co_{0.1}$
1st
2nd
3rd
3rd
2nd
1st
M (emu/g)
15
10
5
0
50
100
150
200
250
300
T (K)

FIG. 8



$Nd_1Si_{0.9}Cu_{0.1}$
1st
2nd
3rd
3rd
1st
2nd
M (emu/g)
20
15
10
5
0
50
100
150
200
250
300
T (K)

FIG. 9

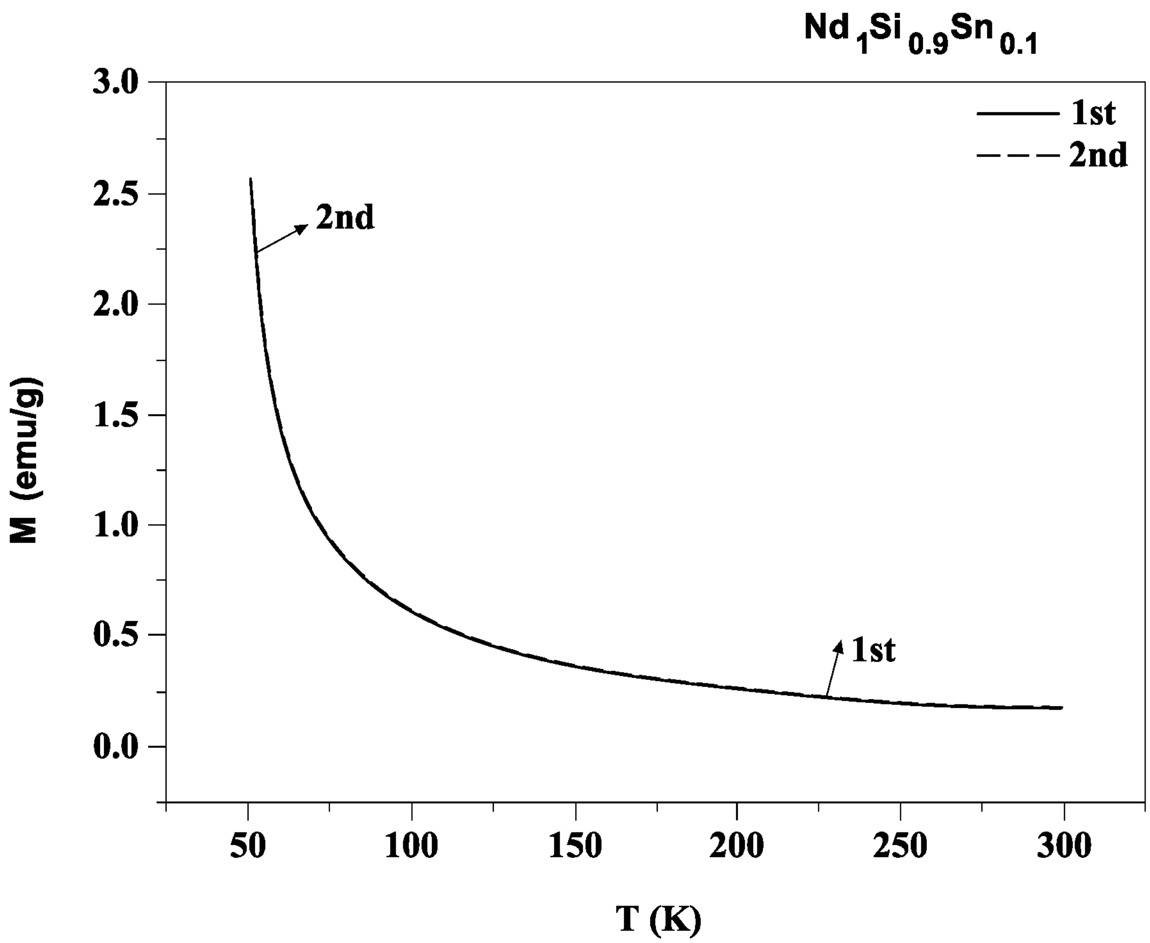

$Nd_1Si_{0.9}Sn_{0.1}$
3.0
2.5
2.0
1.5
1.0
0.5
0.0
M (emu/g)
1st
2nd
2nd
1st
50
100
150
200
250
300
T (K)

FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/012836

A. CLASSIFICATION OF SUBJECT MATTER

[See Supplemental Sheet]

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Databases: PATENW (EPODOC, WPIAP and English full text databases) and WPI. IPC (in PATENW and WPI) and CPC (in PATENW only): H01F, C22C, F25B, C22C 29/18 (and sub-marks), C22C 38/02, C22C 13/00 (and sub-marks), C22C 19/00 (and sub-marks), C22C 45/04, C22C 21/00 (and sub-marks), C22C 45/08, C22C 38/00 (and sub-marks), C22C 45/02, C22C 22/00, C22C 18/00 (and sub-marks), C22C 9/00 (and sub-marks). CPC (in PATENW only): H01F 1/015, H01F 1/012 (and sub-marks), H01F 1/14766 (and sub-marks), H01F 1/15325, C22C 32/0078, C22C 45/008, C22C 45/001, F25B 2321/002. Keywords: magnetocaloric; silicon, silicide; cerium, neodymium, gadolinium; tin, cobalt, aluminium, nickel, iron, manganese, zinc, copper; AND LIKE TERMS. Databases: INSPEC and MEDLINE. Author: Ihnfeldt, Jin, Chen, Xu, Caldwell, Kim. Keywords: magnetocaloric; silicon, silicide; cerium, neodymium, gadolinium; tin, cobalt, aluminium, nickel, iron, manganese, zinc, copper; magnetic; phase change; second; AND LIKE TERMS. Databases: Espacenet and Auspat. Applicant: General Engineering & Research L.L.C, The Regents of the University of California. Inventor: Robin Ihnfeldt, Sungho Jin, Renkun Chen, Xia Xu, Elizabeth Caldwell, Eunjeong Kim. IPC: H01F, C22C, F25B. Keywords: magnetocaloric. Database: Google Scholar. Keywords: magnetocaloric; CeSnSi, NdMnSi, GdMnSi, NdZnSi, CeNdSi, AND LIKE TERMS. Applicant and Inventor names searched in internal databases provided by IP Australia.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 April 2018	23 April 2018

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
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Telephone No. +61262832583

INTERNATIONAL SEARCH REPORT	International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT	**PCT/US2018/012836**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KOWALCZYK A. et al., 'Magnetic, transport and thermodynamic properties of $Ce_5Ni_2Si_3$ compound', Solid State Sciences, 2012, vol. 14, issue 10, pages 1496 to 1502, published online 5 September 2012. Abstract	3, 13-17
X	CHIRIAC H. et al., 'Structure and magnetic properties of some bulk amorphous materials', Journal of Non-Crystalline Solids, 1999, vol. 250-252, part 2, pages 751 to 756, published 1 August 1999 3.2. Hard magnetic materials, 4.2. Hard magnetic materials, Figures 3 to 5	3, 7, 13-15
X	US 6022486 A (TOKAI et al.) 08 February 2000 Column 2 lines 45 to 51, column 6 lines 24 to 40, column 6 line 65 to column 7 line 38, figures 5A to 5C	3, 10-17
X	JP S62-30840 A (NAT RES INST METALS et al.) 09 February 1987, English abstract retrieved from EPODOC database Abstract	3, 13-17
X	Hu, Z et al., 'Magnetocaloric effects in RTX intermetallic compounds (R = Gd - Tm, T = Fe - Cu and Pd, X = Al and Si)', Chinese Physics B, 2015, vol. 24, no. 12, published 10 November 2015. Abstract, 2. MCE in RTSi compounds, 2.1. RFeSi compounds	3, 8, 13-17
X	GUPTA S. et al., 'Review on magnetic and related properties of RTX compounds', Journal of Alloys and Compounds, 2015, vol. 618, pages 562-606, published 5 January 2015. Abstract, 1. Introduction, 3.3 RMnX compounds, 3.4 RFeX compounds, 3.5 RCoX compounds, 3.6 RNiX compounds, 3.7 RCuX compounds, 4. Magnetocaloric effect (MCE), Table II, Table III	3, 5-8, 10-17
A	US 2014/0290274 A1 (HU et al.) 02 October 2014 Abstract, paragraphs 0001, 0007 to 0055, 0072 to 0105, figures 1 to 14	1-17

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:
   the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box for Details

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Supplemental Box

Continuation of: **Box III**
This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 1, 2 and 13 to 17 (to the extent that claims 13 to 17 are ultimately appended to claim 1) are directed to a magnetocaloric material comprising: $(Ce_xNd_{1-x})Si$ wherein x is in the range of about 0.1 to about 0.9, and wherein the magnetocaloric material exhibits a 2nd order magnetic phase transition in the temperature range of about 10K to about 42K. The feature of a magnetocaloric material with the above mentioned features is specific to this group of claims. Please also refer to Box VIII in regards to the construction that has been applied to claims 14 and 15.

- Claims 3 to 17 (to the extent that claims 13 to 17 are ultimately appended to claim 3) are directed to a magnetocaloric material comprising: $RE(Si_yA_{1-y})$ wherein RE is selected from the group consisting of Ce, Nd, or Gd; wherein A is selected from the group consisting of Sn, Co. Al, Ni, Fe, Mn, Zn, or Cu: wherein y is in the range of about 0.1 to about 0.9. The feature of a magnetocaloric material with the above mentioned features is specific to this group of claims. Please also refer to Box VIII in regards to the construction that has been applied to claims 14 and 15.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only features common to all of the claimed inventions and which provides a technical relationship among them are a magnetocaloric material that is a ternary compound or alloy that comprises the element silicon and at least one rare earth element. However these features do not make a contribution over the prior art because they are disclosed in:

KOWALCZYK A. et al., 'Magnetic, transport and thermodynamic properties of $Ce_5Ni_2Si_3$ compound', Solid State Sciences, 2012, vol. 14, issue 10, pages 1496 to 1502, published online 5 September 2012.

See: Abstract.

Therefore in the light of this document these common features cannot be a special technical feature. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a posteriori*.

Supplemental Box – IPC Marks

H01F 1/053 (2006.01)

C22C 9/00 (2006.01)

C22C 13/00 (2006.01)

C22C 18/00 (2006.01)

C22C 19/00 (2006.01)

C22C 21/00 (2006.01)

C22C 22/00 (2006.01)

C22C 28/00 (2006.01)

C22C 29/18 (2006.01)

C22C 38/02 (2006.01)

F25B 21/00 (2006.01)

F25B 30/00 (2006.01)

H01F 1/058 (2006.01)

H01F 1/06 (2006.01)

H01F 1/147 (2006.01)

H01F 1/20 (2006.01)

H01F 1/34 (2006.01)

H01F 1/36 (2006.01)

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/US2018/012836**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 6022486 A	08 February 2000	US 6022486 A	08 Feb 2000
		EP 0327293 A2	09 Aug 1989
		EP 0327293 B1	16 Mar 1994
		JP H10253183 A	25 Sep 1998
		JP 3055674 B2	26 Jun 2000
		JP H0571816 A	23 Mar 1993
		JP H0792286 B2	09 Oct 1995
		JP H01310269 A	14 Dec 1989
		JP H07101134 B2	01 Nov 1995
		US 6336978 B1	08 Jan 2002
JP S62-30840 A	09 February 1987	None	
US 2014/0290274 A1	02 October 2014	None	

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.