AIP Journal of Applied Physics

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Citation: Journal of Applied Physics **113**, 17A916 (2013); doi: 10.1063/1.4795434
View online: http://dx.doi.org/10.1063/1.4795434
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/113/17?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS **113**, 17A916 (2013)

Low hysteresis and large room temperature magnetocaloric effect of $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08, 0.1$) alloys

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(Presented 15 January 2013; received 1 November 2012; accepted 7 December 2012; published online 18 March 2013)

$Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08, 0.1$) alloys were prepared by arc melting followed by annealing at 1273 K for 96 h. Mixed monoclinic $Gd_5Si_2Ge_2$-type phase, orthorhombic Gd_5Si_4-type phase, and a small amount of Gd_5Si_3-type phase were obtained in these alloys. $Gd_5Si_{2.01}Ge_{1.91}Ni_{0.08}$ alloy undergoes a second-order transition (T_C) around 300 K, whereas $Gd_5Si_2Ge_{1.9}Ni_{0.1}$ alloy exhibits two transitions including a first-order transition (T_C^{II}) at ~295 K and second-order transition (T_C^{I}) at ~301 K. Ni substitution can effectively reduce the thermal hysteresis and magnetic hysteresis while maintaining large magnetic entropy change. The maximum magnetic entropy changes ($|\Delta S_M^{max}|$) of $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ alloys with $2x = 0.08$ and 0.1 are 4.4 and 5.0 J kg^{-1} K^{-1}, respectively, for 0–2 T, and are 8.0 and 9.1 J kg^{-1} K^{-1}, respectively, for 0–5 T. Low hysteresis performance and relatively large magnetic entropy change make these alloys favorable for magnetic refrigeration applications. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4795434]

I. INTRODUCTION

As an energy-saving, efficient and eco-friendly cooling technology, magnetic refrigeration is receiving more and more global attention.[1] Various materials[2–7] have been investigated regarding to their applications in this new cooling technology. In particular, discovery of the giant magnetocaloric effect (GMCE) in the $Gd_5(Si_2Ge_2)$ and $Gd_5(Si_xGe_{1-x})_4$ ($0.24 \leq x \leq 0.5$) alloys[2,8] is a benchmark in the study of magnetic refrigerants near room temperature. However, $Gd_5(Si_2Ge_2)$ exhibits large hysteretic loss in the temperature range between 270 and 300 K, which reduces its potential cooling efficiency.[9] As reported earlier, a small amount (total of 0.33 at. %) of Fe, Co, Ni, or Cu substitution for Si and Ge in the $Gd_5Ge_2Si_2$ alloy have significant impact on the maximum value of the magnetic entropy change (ΔS_M) and the Curie temperature (T_C).[10] Among the different 3d metal substitutions, Ni was the one providing the most promising results, as it increases the transition temperature and did not decrease much ΔS_M. Shull and his coworkers found that the addition of Cu, Ga, Mn, and Al completely eliminated the hysteresis loss presented in the undoped $Gd_5Ge_2Si_2$ alloy between 270 and 330 K, broadened the magnetic entropy change (ΔS_M) peak, and shifted its peak position from 275 to 305 K, similar to that observed earlier for $Gd_5Ge_{1.9}Si_2Fe_{0.1}$.[11,12] However, in the case of doping the same amount of either Sn or Bi, a negligible effect on the magnetocaloric properties was evident.[11] Recent results show that partial substitution of Nb in $Gd_5Si_{2-x}Ge_{2-x}Nb_{2x}$ alloys increased T_C to ~295 K and enhanced the magnetocaloric effect as x increased to x = 0.05. The $\Delta S_M = -9.6$ J kg^{-1} K^{-1} for $\Delta H = 2$ T was obtained, which is ~50% higher than that of Nb-free alloy. And microstructure examination indicated that a low amount of detrimental Gd_5Si_3 phase was precipitated.[13] As far as Ni doping is concerned, most previous work focused on the alloy with very low Ni concentrations, typically less than 0.03 at. %.[10] In the present work, $Gd_5Si_{2.05}Ge_{1.95}$ based alloys doped with slightly higher Ni contents were prepared. Their hysteresis behavior, structure, and magnetocaloric properties were investigated.

II. EXPERIMENTS

The alloys with nominal composition of $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$ and 0.1) were prepared by arc melting the raw materials of Gd, Si, Ge, and Ni with purities higher than 99.95 wt. % under argon atmosphere. The ingots were re-melted several times to ensure the composition homogeneity. As-cast ingots were sealed in a quartz tube and annealed at 1273 K for 96 h and subsequently quenched in water. The structural characterization was performed by the X-ray diffractometer (XRD) with Cu-Kα radiation. Magnetic measurements were carried out using a Quantum Design Physical Property Measurement System (model PPMS-9).

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns for the $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) alloys. Three types of phases, i.e., monoclinic $Gd_5Si_2Ge_2$-type phase, orthorhombic Gd_5Si_4-type phase, and hexagonal $Gd_5(Si,Ge)_3$-type phase, were observed. The XRD peaks at ~26.2° and 37.9°

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0021-8979/2013/113(17)/17A916/3/$30.00

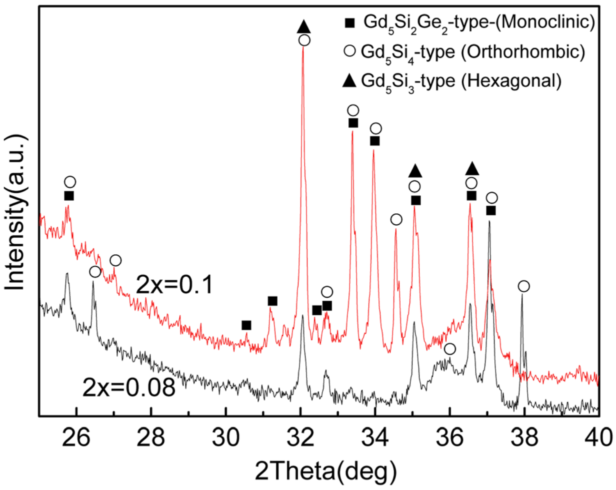

FIG. 1. The XRD patterns for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) alloys at room temperature.

corresponding to 5:4-type phase were present on the pattern of $2x = 0.08$ sample, but absent on that of $2x = 0.1$ sample. The XRD peaks at ∼31.2° and 32.4° correspond to the monoclinic $Gd_5Si_2Ge_2$-type phase. The result also indicates that the content of Ni-substitution has an effect on the formation of 5-2-2 phase. With increasing Ni content from ∼0.89 ($2x = 0.08$) to ∼1.11 at. % ($2x = 0.1$), the amount of orthorhombic Gd_5Si_4-type phase decreases and the amount of monoclinic $Gd_5Si_2Ge_2$-type phase increases. The XRD peaks at ∼35.2° and ∼36.6° in Fig. 1 are related to the hexagonal $Gd_5(Si, Ge)_3$-type phase.

The temperature dependencies of magnetization for the $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) alloys measured in an applied field of 0.05 T between 5 and 300 K under field cooling (FC) and field heating (FH) conditions are shown in Fig. 2. The T_C was defined as the temperature at the maximum of $|dM/dT|$ vs T plot based on FH curve. The lack of thermal hysteresis in $Gd_5Si_{2.01}Ge_{1.91}Ni_{0.08}$ alloy indicates that it should undergo a second-order magnetic transition, and T_C is around 300 K. For $Gd_5Si_2Ge_{1.9}Ni_{0.1}$, two slopes are observed in M-T curves, indicating two magnetic transitions, a first-order transition (T_C^{II}) at ∼295 K and a second-order transition (T_C^{I}) at ∼301 K. It is also found that the thermal hysteresis between FC and FH curves is negligible for $2x = 0.08$ alloy, whereas that is ∼6–13 K for $2x = 0.1$. A similar behavior was observed for the magnetic hysteresis in the magnetic isotherms for the experimental alloys, as will be discussed later.

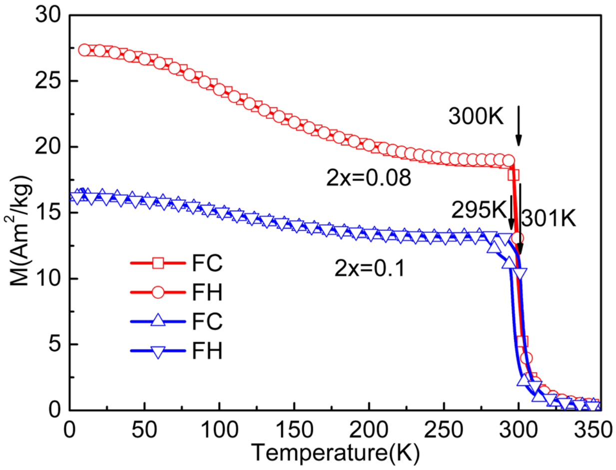

FIG. 2. Magnetization–temperature curves for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) alloys measured in a magnetic field of 0.05 T.

Figure 3 displays the isothermal magnetization curves for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, and 0.1) alloys. The $Gd_5Si_2Ge_{1.9}Ni_{0.1}$ alloy (Fig. 3(b)) has the typical magnetization characteristics of pure $Gd_5Si_2Ge_2$ for the temperatures above T_C^{I} (∼ 301 K). We can see a typical field induced transition from the PM to the field-induced ferromagnetic state. Combined with partial magnetic hysteresis with respect to a reversed magnetic field, this shows that the transitions are first order. The transition occurs at higher field values with increasing temperature in the range between 288 K and 324 K. As already stated, it has been hypothesized that this transition is the result of a field-induced first-order crystallographic phase change from the paramagnetic monoclinic phase to a ferromagnetic orthorhombic phase,[14] which results in the peak of ($-\Delta S_M$) for $Gd_5Si_2Ge_{1.9}Ni_{0.1}$ alloy shifting ∼290 K at low field ($\Delta\mu_0 H = 2.0$ T) to ∼300 K at high field ($\Delta\mu_0 H = 5.0$ T) (shown in Fig. 4). The $Gd_5Si_{2.01}Ge_{1.91}Ni_{0.08}$ alloy (Fig. 3(a)),

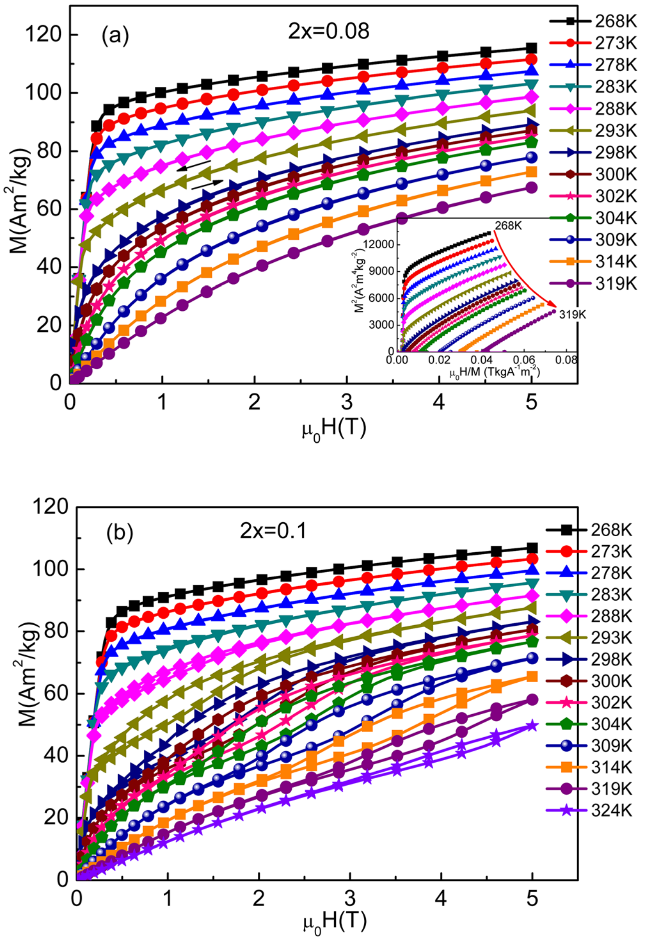

FIG. 3. Field dependencies of magnetization of $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) compounds measured with increasing field and decreasing field in maximum fields up to 5 T. The inset of the lower right corner of Fig. 3(a) shows the Arrott plots of the $Gd_5Si_{2.01}Ge_{1.91}Ni_{0.08}$ alloy.

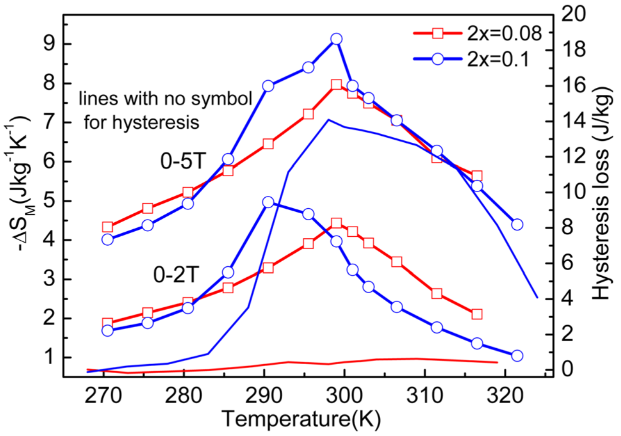

FIG. 4. Temperature dependencies of magnetic entropy change and hysteresis loss for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) compounds. Hysteresis loss is plotted for the magnetic-field change from 0 to 5 T.

however, has lost the two-step magnetic ordering and shows negligible hysteresis, and it performs as a typical ferromagnet. The Arrott plots of the $Gd_5Si_{2.01}Ge_{1.91}Ni_{0.08}$ alloy are displayed in the inset of Fig. 3(a). No inflection or negative slope is observed as an indication that FM–PM transition is of second-order.[15,16]

The magnetic-entropy changes ($-\Delta S_M$) were calculated based on the magnetic isotherms in the vicinity of T_C using the Maxwell relation. The ($-\Delta S_M$) vs T plots of the $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ alloys are presented in Fig. 4. The maximum magnetic entropy change ($|\Delta S_M^{max}|$) for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ with $2x = 0.08$ and 0.1 is 4.4 and 5.0 J kg^{-1} K^{-1}, respectively, for the applied-field change of 0 to 2 T. The $|\Delta S_M^{max}|$ is 8.0 and 9.1 J kg^{-1} K^{-1}, respectively, for 0 to 5 T. These values are comparable to that of pure Gd (5.1 J kg^{-1} K^{-1} at $\Delta\mu_0 H = 2.0$ T and 10.2 J kg^{-1} K^{-1} at $\Delta\mu_0 H = 5.0$ T). Refrigerant capacity (RC) as another effective criterion for characterizing the refrigerant efficiency could be estimated by the method of Gschneidner.[17] When the applied field changed from 0 to 2 T, RC values of $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ with $2x = 0.08$ and 0.1 are 122 and 90 J kg^{-1}, respectively. The RC value under an applied field change of 5 T for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.1$) alloy is 288 J kg^{-1}, which is slightly smaller than that of $Gd_5Si_2Ge_2$ (305 J kg^{-1}, $\Delta\mu_0 H = 5.0$ T).[12] One way to take into account the hysteresis loss of each alloy is to simply subtract it from the corresponding RC value.[12] From Fig. 4, the value of magnetic hysteresis loss for $2x = 0.08$ compound is calculated as less than 1 J/kg and the maximum magnetic hysteresis loss for $2x = 0.1$ alloy is about 14 J/kg. Both values are much smaller than that of the $Gd_5Si_2Ge_2$ (average value is about 65 J/kg). The low hysteresis with relatively large magnetic entropy change for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) alloys is favorable for the applications of magnetic refrigeration materials.

IV. CONCLUSIONS

Ni substituted $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ alloys ($2x = 0.08$ and 0.1) exhibit multiphase structure. The Curie temperature for second order transition of the alloys with $2x = 0.08$ and 0.1 is 300 and 301 K, respectively. An obvious first order transition is exhibited around 295 K for $2x = 0.1$ compound. The maximum of magnetic entropy change ($|\Delta S_M^{max}|$) of $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ alloys with $2x = 0.08$ and 0.1 is 4.4 and 5.0 J kg^{-1} K^{-1}, 8.0 and 9.1 J kg^{-1} K^{-1}, respectively, under an applied field changes from 0 to 2 T and 0 to 5 T, respectively. The thermal and magnetic hysteresis behaviors are negligible in $2x = 0.08$ alloy. Though thermal hysteresis is ∼6–13 K for the alloy with $2x = 0.1$, the maximum magnetic hysteresis loss is only about 14 J/kg around transition temperature. This study extends the range of Ni doping in GdSiGeX, as well as focuses on compositions with Si:Ge ratios larger than one, which can be beneficial for magnetic refrigeration applications. Low hysteresis and large ΔS_M suggest that $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ alloys ($2x = 0.08$ and 0.1) be good candidates for magnetocaloric materials working at room temperature.

ACKNOWLEDGMENTS

This work was financially supported by the Guangzhou Municipal Science and Technology Program (Grant No. 12F582080022), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (Grant No. x2clB7120290), the Fundamental Research Funds for the Central Universities, (Grant Nos. 2011ZM0014 and 2012ZZ0013), and the Guangdong Provincial Science and Technology Program (Grant Nos. 2010B050300008 and 2009B090300273).

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