Magnetocaloric Properties and Structure of the $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ Compund

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In this study the magnetic properties and the structure of $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ alloy were investigated by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and magnetometry. The concentration of the Sn-doping in this study is four times that used in previous studies examining the magnetocaloric properties of the $Gd_5Ge_2Si_2$ compound doped with different metal additives. In the earlier studies it was shown the addition of about one atom percent of either Fe, Cu, Co, Ga, Mn, or Al nearly eliminated the large hysteresis losses present in the undoped $Gd_5Ge_2Si_2$ compound between 270 K and 300 K. Also, these metal additives affected the characteristics ΔS_m versus T peak, resulting in a significant increase in the refrigeration capacity of the material, if the hysteresis losses are taken into account. By contrast, the same amount of either Sn or Bi had much smaller effects on both the hysteresis losses and the characteristics of the ΔS_m versus T peak. In this study, a larger amount of Sn doping had a limited effect on the hysteresis losses and characteristics of the ΔS_m versus T peak of $Gd_5Ge_2Si_2$. But, most importantly, it resulted in a different microstructure compared to the compound with smaller Sn addition. The implications of the larger Sn doping on both the magnetocaloric properties and structure of the $Gd_5Ge_2Si_2$ compound are discussed.

Index Terms—**Field-induced transition, hysteresis losses, magnetocaloric properties, Sn-doped GdGeSi compound.**

I. Introduction

SINCE the late 1990s, a great deal of attention has been focused on the $Gd_5Ge_2Si_2$ compound as a potential near room temperature magnetic refrigerant due to its large so called "giant" magnetocaloric effect (magnetic entropy change, ΔS_m) between 270 K and 300 K [1]–[4]. Unfortunately, this compound also possesses large hysteretic losses in this same temperature range, thereby reducing its efficiency as a refrigerant [3], [4]. However, Provenzano and his coworkers at NIST first showed that doping the $Gd_5Ge_2Si_2$ compound with about 1 atom percent of iron not only greatly decreased the large hysteresis losses (>90%) but also improved the characteristics of its magnetocaloric ΔS_m peak. In fact, compared to the undoped case, the Fe-doped compound displayed a broader peak with its peak value shifted from 275 to 305 K together with a 20%–50% improvement in the refrigeration capacity value, if the hysteresis losses are taken into account [5]. The NIST group also studied the effect of other metal additives to the $Gd_5Ge_2Si_2$ compound. From this subsequent study, the NIST group observed that the effect of doping the compound with about one atom% of either Al, Co, Cu, Ga, or Mn was very similar to that which had been observed with the Fe-doping. However, in the case of doping with the same amount of either Sn or Bi, a negligible effect on the magnetocaloric properties was observed [6]. This work is a follow up study to the earlier studies for the purpose of examining the effect of larger amounts of doping on the structure and magnetocaloric properties of the $Gd_5Ge_2Si_2$ compound. Here we present the magnetic and microstructural results of doping the $Gd_5Ge_2Si_2$ compound with about 4.5 atom% Sn; this doping level is 4 times the doping level of our earlier study [5], [6].

II. Experimental Procedure

The $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ sample of this study was prepared by arc melting as in the previous studies, using a water-cooled copper hearth in an argon atmosphere starting with the appropriate amounts of the component elements. The purity of the starting constituents was 99.9% mass fraction or better, and prior to microstructural characterization and magnetic measurements the sample was homogenized for 1 h at 1300 °C in vacuum. This is the same heat treatment previously used on the $Gd_5Ge_2Si_2$ compound doped with different metal additives. The sample microstructure was examined by appropriate electro-optical techniques, including X-ray Diffraction Spectroscopy (XRD), Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS), while its magnetocaloric properties were characterized by SQUID magnetometry.

III. Results and Discussion

Fig. 1 shows the room temperature X-ray powder diffraction spectra of the Gd_5Si_4 (A) and the $Gd_5Ge_2Si_2$ (B) compounds and of the $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ alloy (C); the spectrum of the Gd_5Si_4 compound is analogous to that of $Gd_5Ge_2Si_2$ below the orthorhombic-to-monoclinic phase transition temperature.

Thus, Fig. 1(a) and (b) illustrates respectively the typical orthorhombic and monoclinic crystal structures of the undoped $Gd_5Ge_2Si_2$ compound below and above the phase transition temperature of 270 K to 275 K. On the other hand, Fig. 1(c) shows that the X-ray diffraction peaks of the Sn-doped compound closely match those of the monoclinic phase, with the exception of a slight shift of the peaks to lower angles. This suggests that, at room temperature, the Sn-doped compound has a monoclinic structure similar to that of the undoped compound, but it has a slight increase in the lattice parameters. The lattice parameter values of the three crystal phases of Fig. 1 are given in Table I.

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TABLE I
LATTICE PARAMETERS COMPARISON

	a	b	c	γ	Volume	S.G.	Structure Type
Gd_5Si_4	7.48570	14.75000	7.75140	90	855.93	62	Orthorhombic
$Gd_5Si_2Ge_2$	7.58085	14.8021	7.77995	93.190	871.62	14	Monoclinic
$Gd_5Si_{1.8}Ge_{1.8}Sn_{0.4}$	7.5868(1)	14.8247(1)	7.7876(5)	92.764(2)	874.87(4)	14	Monoclinic

The data for Gd_5Si_4 and $Gd_5Si_2Ge_2$ were taken from [8].

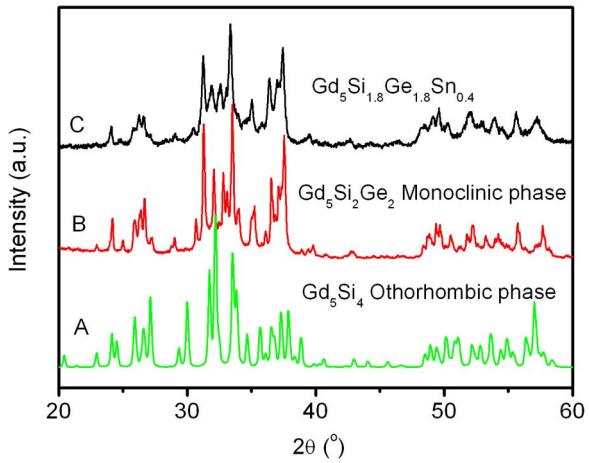

Fig. 1. Room temperature X-ray diffraction spectra of: (A) Gd_5S_4 (orthorhombic phase), (B) $Gd_5Ge_2Si_2$ (monoclinic phase), and (C) $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ compound.

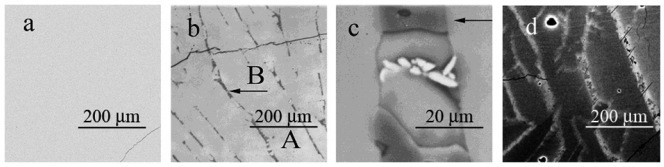

Fig. 2. Backscattered scanning electron micrographs showing typical microstructures of (a) $Gd_5Ge_2Si_2$, (b) and (c) $Gd_5Ge_{1.9}Si_2Cu_{0.1}$, (d) $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ compounds; all the samples were heat treated in vacuum at 1300 °C for 1 h.

The results of the X-ray diffraction analysis are consistent with both the corresponding microstructure (examined by SEM and EDS element analysis) and with the magnetic property results. The SEM micrographs shown in Fig. 2 illustrate the typical microstructure of the undoped $Gd_5Ge_2Si_2$ compound (panel a) and the alloys doped with Fe (panels b and c) and with Sn (d). From the SEM micrographs in Fig. 2 and from the corresponding EDS chemical analyses, consistent with X-ray results, mentioned above, Fe-doping resulted in a microstructure that consisted of a majority phase and a minority phase rich in Fe and Si [Fig. 2(b), (c)] [7].

The undoped compound, however, consisted of only the single $Gd_5Ge_2Si_2$ phase [Fig. 2(a)]. On the other hand, the Sn-doped alloy displayed a dark majority phase and a light-colored phase where some of the Sn had segregated away from the majority phase. Though not shown here, the microstructure of the compound with the smaller amount of Sn doping (∼1 atom%) displayed only the single $Gd_5Ge_2Si_2$ phase with no secondary Sn segregated to a secondary phase. Taken together the X-ray diffraction and microstructural results of the alloy with the two different amounts of Sn doping, as it will be discussed later, seem to suggest that for case of the larger doping, not all the Sn atoms were accommodated substitutionally in the crystal lattice of $Gd_5Ge_2Si_2$ compound. Consequently, the excess atoms segregated and were incorporated into a secondary phase. As it will be discussed further, about half of the Sn atoms reside within the $Gd_5Ge_2Si_2$ crystal lattice, while the other half is segregated. On the other hand, for the case of the smaller doping, nearly all the Sn atoms reside within the crystal lattice of the compound.

In Fig. 3, the M versus H loops measured at various temperatures for the Sn-doped alloy [Fig. 3(a)] of the present study are compared to those of the alloy containing a smaller amount of tin [≈1 atom%, Fig. 3(b)] from the earlier study [8], in the 260 K to 320 K temperature range. Both sets of loops show the presence of hysteresis and the amount of hysteresis loss as a function of temperature is roughly the same for both Sn-doped alloys (Fig. 4).

In Fig. 5(a) and (b) are shown respectively the M versus T data and the entropy change, ΔS_m, versus T plot for a $\Delta H = 3980$ kA/m (5 T) of the following: $Gd_5Ge_2Si_2$ $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$, and $Gd_5Ge_{1.9}Si_2Cu_{01}$ alloys.

The M versus T plots for both the $Gd_5Ge_2Si_2$ compound and the $Gd_5Ge_{1.9}Si_2Cu_{01}$ alloy were obtained at a constant field value of 796 kA/m (1 T), whereas that for the $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ alloy was measured at 79 kA/m (0.1 T). Fig. 5(a) shows a sharp transition around the Curie temperature for the undoped $Gd_5Ge_2Si_2$ compound, occurring at the orthorhombic-to-monoclinic crystal phase transition (≈275 K). Fig. 5(a) also shows a smooth ferromagnetic-to-paramagnetic smooth transition at T_C for the Cu-doped $Gd_5Ge_{1.9}Si_2Cu_{01}$ alloy (≈305 K) and a not too sharp transition at T_C for the Sn-doped $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ alloy (≈245 K). Thus, with respect to the undoped compound, the Sn-doped alloy exhibits a smoother transition and a lower Curie temperature. Consistent with the M versus T plots, the ΔS_m versus T peak for each is centered at its corresponding Curie temperature [Fig. 5(b)], but with varying heights and peak widths. The smoother transition and a smaller but broader ΔS_m peak of the Sn-doped alloy are accompanied by smaller hysteresis, as compared to those of the undoped compound [5], [6]. When the hysteresis losses (Figs. 3 and 4) are taken into account and the net refrigeration capacity (RC_{NET}) is calculated by the method outlined in [7] and using the integrals of the ΔS_m versus T plots of Fig. 5(b), a RC_{NET} of about 340 J/kg-K for $\Delta H = 3980$ kA/m (5 T) was computed for the $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ alloy. This value is similar to the RC_{NET} values computed for the other metal additives [6]. However, the RC_{NET} value for the alloy with the smaller amount of Sn doping (∼1 atom%) was only 260 J/kg-K, which is close to that of the undoped compound [5], [6].

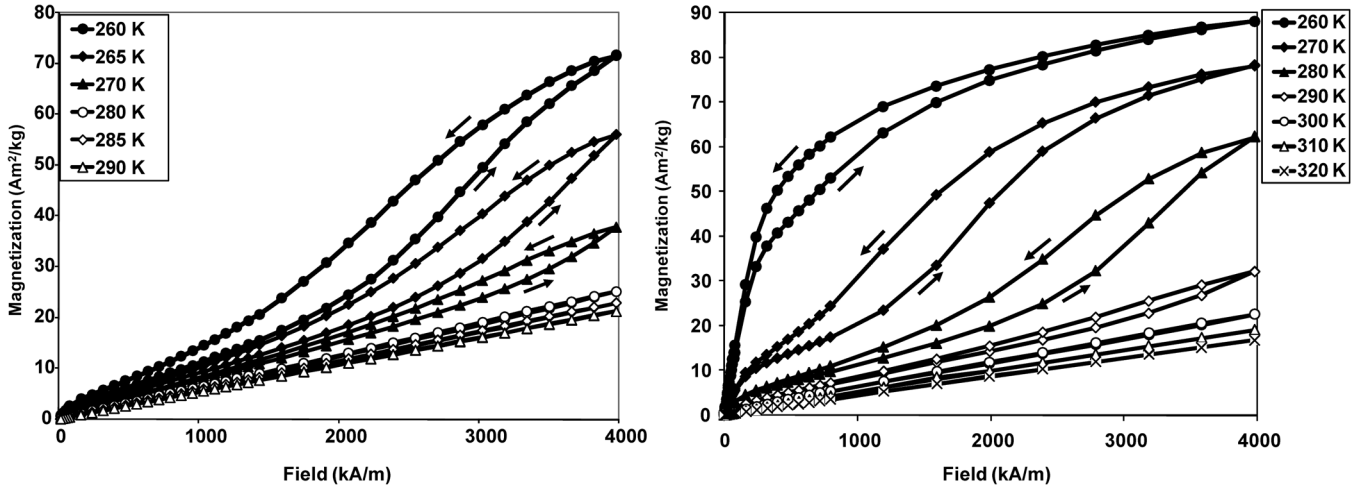

Fig. 3. M versus H loops for $Gd_5Ge_{1.8}$ $Si_{1.8}Sn_{0.4}$ (right) and $Gd_5Ge_{1.9}$ $Si_2Sn_{0.1}$ (left) compounds.

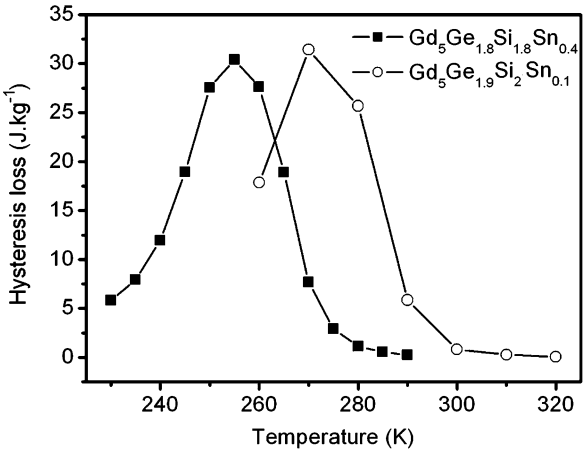

Fig. 4. Hysteresis loss versus temperature plots for the $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ and $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.1}$ alloys.

Quantitative analysis results that were obtained from the SEM micrographs and the corresponding EDS area maps (not shown) indicated that about half of the tin in the alloy was contained in the minority phase. From the EDS analysis and X-ray diffraction results it was concluded that the other half of the Sn atoms reside substitutionally in the $Gd_5Ge_2Si_2$ lattice. These results obtained for the $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ alloy reinforce the previous conclusions from the study on alloys containing smaller amounts of metal doping [5], [6]. These conclusions stated that small amounts of non-Sn or Bi doping nearly eliminate the large hysteresis losses in the $Gd_5Ge_2Si_2$ compound while at the same time significantly changing the characteristics of its ΔS_m versus T peak. This is because the presence of the doping metal suppresses the reversible field-induced first-order monoclinic-to-orthorhombic phase transition in the compound between 270 K and 300 K temperature range [7]. That is, the metal doping causes a retention of the orthorhombic phase by partially depleting the silicon in the $Gd_5Ge_2Si_2$ compound as an additional minority phase is formed that is rich of both silicon and the doping metal. On the other hand, the present results obtained on the $Gd_5Ge_2Si_2$ compound containing a higher level of Sn doping clearly show that the field-induced monoclinic-to-orthorhombic phase transition is not entirely suppressed. Consequently, even the higher amount of Sn doping did not result in the complete retention of the orthorhombic phase. This is because there is still sufficient silicon present in the majority phase to keep it from forming the orthorhombic structure at high temperatures, while the Sn containing minority phase was being formed. This result is consistent with the elemental analysis maps of the $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ alloy which showed the observed minority phase contained little Si. Therefore, the appearance of the minority phase in the present Sn-doped alloy does not signify a depletion of Si in the majority phase as occurred for the case of the $Gd_5Ge_2Si_2$ compound doped with either Fe, Cu, Ga, Mn, Co, or Al [5], [6]. Therefore, the higher Sn doped alloy of the present study still displayed the large hysteresis loss similar to that of the $Gd_5Ge_2Si_2$ alloy containing a smaller amount of Sn doping [6]. Consistent with the retention of relatively large amount of hysteresis loss in the Sn doped alloy of the present study, there was not a large reduction in the magnetocaloric effect peak height, compared to that computed for the $Gd_5Ge_2Si_2$ compound [5].

IV. Conclusion

The present study conducted on the $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ Sn-doped compound re-enforces the previously stated hypothesis that the formation of a minority phase, rich both in Si and of the corresponding doping element (with attendant partial depletion of Si in the parent majority phase), is the key for eliminating the hysteresis losses in the $Gd_5Ge_2Si_2$ compound because the partial depletion of Si suppressed the reversible field-induced orthorhombic-to-monoclinic crystal phase transition. In fact, comparison of the X-ray diffraction spectra, taken at temperatures considerably below the phase transition temperature with a spectrum measured at room temperature on the Fe-doped compound showed that in the range of temperature from 2 K to 350 K (where the magnetic measurements data were taken), the Fe-doped alloy retained the orthorhombic crystal structure and thus the orthorhombic-to-monoclinic crystal phase transition did not occur [7], [8], [9]. Consequently, the reversible field-induced monoclinic-to-orthorhombic phase transition,

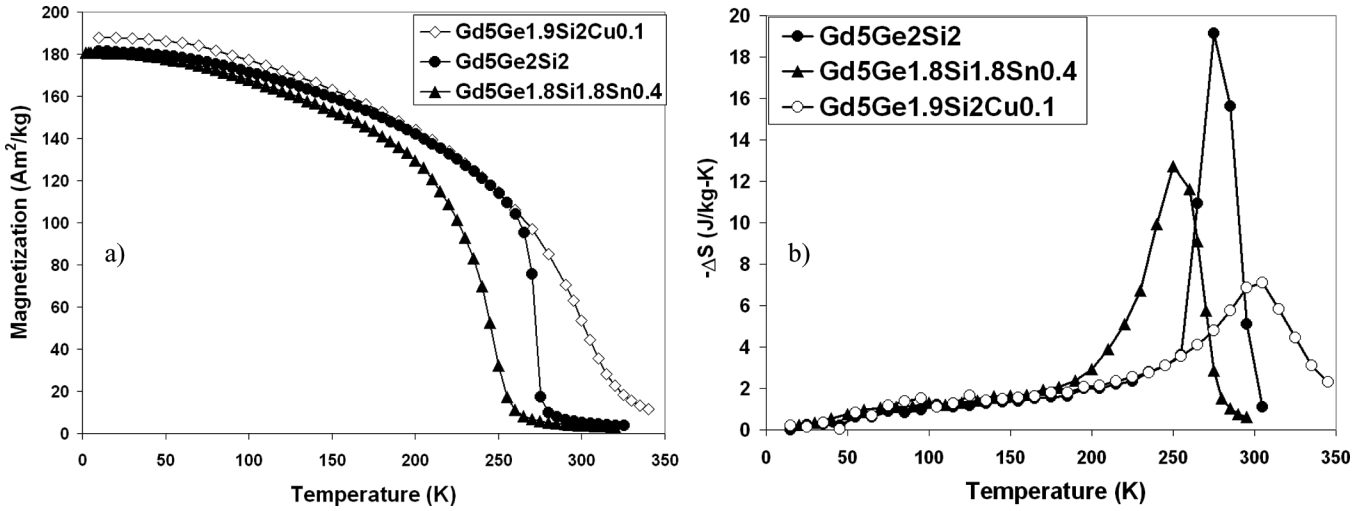

Fig. 5. (a) M versus T plots at 796 kA/m (1 T) constant field for $Gd_5Ge_2Si_2$ compound, $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ and $Gd_5Ge_{1.9}Si_2Cu_{0.1}$ alloys. (b) $-\Delta S$ versus T plot for $\Delta H = 3980$ kA/m (5 T) for $Gd_5Ge_2Si_2$ compound and $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$, and $Gd_5Ge_{1.9}Si_2Cu_{0.1}$ alloys.

observed in the dopant-free compound, was also suppressed. On the other hand, the presence of hysteresis losses observed in the Sn-doped compound indicates that the reversible monoclinic-to-orthorhombic field-induced phase transition is only partially suppressed. The SEM and EDS results together with observed slight increase in the crystal lattice parameter values (determined from the X-ray diffraction data), suggests that about half of the Sn atoms in the $Gd_5Ge_{1.8}Si_{1.8}Sn_{0.4}$ compound reside substitutionally in the Ge-Si crystal lattice sites.

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