Effect of B alloying on magnetocaloric effect of Gd$_{5.1}$Si$_2$Ge$_2$ alloy in low magnetic field

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Abstract: A series of the Gd$_{5.1}$Si$_2$Ge$_2$$_x$B$_x$ alloys were prepared with arc melting in purified argon atmosphere. The effect of B addition on the magnetocaloric effect of compound Gd$_5$Si$_2$Ge$_2$ was investigated by powder X-ray diffraction technology and DSC and direct magnetocaloric effect apparatus and vibrating sample magnetometer (VSM). The results show that the addition of a small amount of B maintains the Gd$_5$Si$_2$Ge$_2$ compound in single monoclinic phase with superior magnetocaloric effect, especially when $x$=0.01, the maximum magnetic entropy change ($|\Delta S_M|$) reaches the values of 13.7 J/(kg·K) at 288 K in 1.5 T magnetic field. With the increase of B content, some orthorhombic Gd$_5$Si$_4$-type phases appear in the matrix of monoclinic Gd$_5$Si$_2$Ge$_2$-type phase in Gd$_{5.1}$Si$_2$Ge$_2$$_x$B$_x$ alloys.

Key words: B-doping; Gd$_{5.1}$Si$_2$Ge$_2$; crystal structure; magnetocaloric effect; adiabatic temperature change; magnetic entropy change

1 Introduction

Magnetic refrigeration technology is considered to have great potential to be developed as a green refrigeration technology in the 21st century to replace the traditional refrigeration technology since it has the advantages of high efficiency, energy-saving, limited noise and no greenhouse effect [1–4]. Magnetic refrigeration materials are the key issues for the application of the magnetic refrigeration technique. Once the room magnetic refrigeration technology is put into use, its marketing perspective is worth expected [5]. This makes the development of room magnetic materials with giant magnetocaloric effect into hot issue in the world.

The discovery of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$(0.24$<x$<0.5) alloys is the most important breakthrough in the fields of magnetic refrigerating materials [6–8]. The Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ series alloys have giant magnetocaloric effect, its Curie temperature may be adjusted among in the range from 30 K to 300 K by tuning the ratio of Si/Ge, which makes the magnetic refrigeration technology have the possibility to come true. However, there still exist some problems for the alloys, such as, too low Curie temperature ($T_C$), the narrow span of cooling temperature, etc. Therefore, the material scientists are making great efforts to search for suitable element to replace Si or Ge in order to improve Curie temperature and broaden the span of refrigerating temperature. Many elements have been used as the alloying element for the Gd$_5$Si$_2$Ge$_2$ alloy, but the effect of B element on the magnetocaloric effect of Gd$_5$Si$_2$Ge$_2$ alloy has still not been studied. In order to improve Curie temperature and broaden the span of refrigeration temperature, the influence of the B addition on the magnetocaloric effect for compound Gd$_{5.1}$Si$_2$Ge$_2$ was studied.

The Curie temperature ($T_C$) of Gd$_5$Si$_2$Ge$_2$ alloy measured in Ames Laboratory is 276 K which is lower and narrower than that of refrigeration materials. Comparing with Gd$_5$Si$_2$Ge$_2$ alloy, nonstoichiometric Gd$_5$Si$_2$Ge$_2$ alloy is more suitable as magnetic refrigeration materials. Therefore, the magnetocaloric effect of Gd$_{5.1}$Si$_2$Ge$_2$ compound doped by B was studied in this work.

2 Experimental

The Gd$_{5.1}$Si$_2$Ge$_2$$_x$B$_x$ ($x$=0, 0.01, 0.03, 0.05, 0.10, 0.15) series alloys, with 99.9% Gd and 99.99% Si, Ge and 99.999%B (mass fraction), were prepared by arc-
melted method under argon atmosphere in WK-II vacuum electric arc furnace with non-consuming tungsten electrode. In the melting process, each button was re-melted five times to ensure the homogeneity.

The phase composition and crystal structure of each sample were analyzed by X-ray diffraction using Cu Kα radiation on the Rigaku D/max 2500 V diffractometer. The melted buttons were cut into 5 mm×5 mm×2 mm samples in order to measure their adiabatic temperature change in 1.2 T external magnetic fields using direct magnetocaloric effect measuring apparatus.

The magnetic transition temperatures and phase transformation behavior were measured using differential scanning calorimeter (TA Instruments−Q2000 DSC) with a scanning rate of 20 K/min under nitrogen atmosphere.

The thermomagnetic curves (M−T) under 0.1 T and isothermal magnetization curves (M−H) from 0 to 1.5 T were measured by vibrating sample magnetometer (VSM) in order to infer the Curie temperatures (Tc) and the isothermal magnetic entropy change was calculated by magnetization curves nearby Tc. The magnetic entropy change (|∆SM|) can be numerically calculated by [7]:

\[
\Delta S_M \left( \frac{T_{s+1} + T_s}{2} \right) = \sum_f \frac{(M_s - M_{s+1}) H_f}{T_s - T_{s+1}} \Delta H
\]

where \(M_s\) and \(M_{s+1}\) represent the values of the magnetization in a magnetic field \(H\) at temperatures \(T_s\) and \(T_{s+1}\), respectively.

3 Results and discussion

Figure 1 shows the XRD patterns of Gd_{5.1}Si_{2}Ge_{2−x}B_{x} alloy. The results prove that as-cast Gd_{5.1}Si_{2}Ge_{2} alloy is crystallized as the Gd_{5}Si_{2}Ge_{2}-type monoclinic structure. Compared with the standard Gd_{5}Si_{2}Ge_{2} PDF card, the peaks of Gd_{5.1}Si_{2}Ge_{2} alloy slightly shift toward the lower angle, but still maintain the Gd_{5}Si_{2}Ge_{2}-type monoclinic structure with space group of \(P112_1/a\). It has been obviously seen that the small substitution of Ge by B does not change Gd_{5}Si_{2}Ge_{2}-type monoclinic structure for Gd_{5.1}Si_{2}Ge_{2}B_{x} alloy, especially when \(x=0.01\) there almost only exists single monoclinic phase which is clearly superior to the magnetocaloric effect. With the increasing addition of element B, orthorhombic Gd_{3}Si_{2}Ge_{2} type structure phase appears in the parent phase, when \(x=0.15\) there almost only exists orthorhombic phase which is inferior to the magnetocaloric effect.

Figure 2(a) shows the DSC curves of all samples. Fig. 2(b) shows two endothermic peaks in Gd_{5.1}Si_{2}Ge_{2} compound without B addition, where the first sharp endothermic peak at 273 K corresponds to the first order transition of the monoclinic Gd_{5}Si_{2}Ge_{2}-type phase while the second endothermic peak with the small step at 300 K corresponds to the order-disorder magnetic phase transition of orthorhombic Gd_{3}Si_{2}Ge_{2}-type phase (the second order transition) [9]. It is reasonable to believe that the orthorhombic Gd_{3}Si_{2}Ge_{2}-type phase exists with monoclinic Gd_{5}Si_{2}Ge_{2}-type phase in Gd_{5.1}Si_{2}Ge_{2} compound without B addition, but the content of Gd_{3}Si_{2}Ge_{2}-type phase is too
minor to be found in Fig. 1. With the addition of trace amount of B for Ge, Fig. 2 shows that the endothermic peak becomes sharp and there is only one endothermic peak in Gd_{5.1}Si_{2}Ge_{2−x}B_{x} (x=0.01) alloys, indicating that the second order transition disappears and only the first order transition occurs in the alloy. This is in good agreement with that in Fig. 1 (x=0.01). This also indicates that the trace amount B-doping in Gd_{5.1}Si_{2}Ge_{2} compound is beneficial to the formation of Gd_{5.1}Si_{2}Ge_{2-type} phase.

The temperature dependence of the magnetization of Gd_{5.1}Si_{2}Ge_{2-x}B_{x} series alloys was investigated under a field of 0.1 T. A representative measurement result (x=0.01) is presented in Fig. 3(a). The Curie temperature was determined as the temperature where the first derivative of the magnetization with respect to temperature has an extreme shown Fig. 3(a). Fig. 3(b) shows the composition dependence of the Curie temperature of the Gd_{5.1}Si_{2}Ge_{2-x}B_{x} series alloys. Upon substitution of B for Ge, the Curie temperature increases linearly with B content from 285 K for x=0 to 303 K for x=0.15, i.e., the Curie temperature of the compound is increased by 18 K when the content changes from Gd_{5.1}Si_{2}Ge_{2} to Gd_{5.1}Si_{2}Ge_{2.015}B_{0.15}, which makes Gd_{5.1}Si_{2}Ge_{2} compound by B-doping enters ideal temperature range of room temperature magnetic refrigeration.

According to BLEANEY et al [10], the effective exchange interaction within the Ruderman-Kittel-Kasuya-Yosida (RKKY) and the magnetic ordering temperature can be expressed as follows:

\[
T_c = \frac{3\pi n^2}{K F} J_{sd}^2 (g - 1)^2 J (J + 1) \sum_{i<j} F(2K_{s}R_{ij})
\]

where \(F\) and \(K\) are the Fermi energy and Fermiwave vector of the s-conduction electrons, respectively; \(K\) is Boltzmann constant; \(n\) is the average number of conduction electrons per atom; \(J_{sd}\) is the s−f exchange integral; \(F(2K_{s}R_{ij})\) is a spherical oscillating function of \(R_{ij}\) and \(R_{ij}\) is the interatomic distance of magnetic atoms.

Eq. (2) indicates that the compound with shorter \(R_{ij}\) and higher conduction electron concentration \(n^2\) will have higher magnetic ordering temperature [10]. \(T_c\) is mainly affected by the indirect exchange interaction of magnetic Gd atoms in Gd_{5}Si_{2}Ge_{2} alloy. But the bond distance of (Si, Ge)−(Si, Ge) covalent bond aslo strongly affects RKKY interaction among Gd atoms. In this experiment, the atomic radius of doping element B (0.117 nm) is smaller than that of Si (0.146 nm) or Ge(0.152 nm), therefore, when B substitutes Si or Ge and enters the crystal lattice of the compound, the bond distance of (Si, Ge)−(Si, Ge) covalent bond will reduce and RKKY interaction will be enhanced, making \(T_c\) of Gd_{5.1}Si_{2}Ge_{2-x}B_{x} alloys increase with the addition of element B.

The isothermal magnetization curves (M−H) across the Curie temperature were measured by VSM at \(\Delta H = 1.5\) T in order to determine the magnetic-entropy changes (\(\Delta S_{ad}\)) in Gd_{5.1}Si_{2}Ge_{2-x}B_{x} series alloys. The magnetic-entropy changes have been derived from the magnetization data on the basis of Eq. (1) by the dependence of the magnetization at different temperatures across the Curie temperature. A representative measurement result (x=0.01) is presented in Fig. 4. The results of the \(\Delta S_{ad}\) for all samples in magnetic field range from 0 to 1.5 T are shown in Fig. 5 and Table 1.

The temperature dependence of the maximum adiabatic temperature change (\(\Delta T_{ad}\)) for Gd_{5.1}Si_{2}Ge_{2-x}B_{x} alloys at \(\Delta H = 1.2\) T is presented in Fig. 6. When the content of B is low (x=0.01), \(\Delta T_{ad}\) is almost the same as that of Gd_{5.1}Si_{2}Ge_{2} alloy, but the temperature range of the \(\Delta T_{ad}\) is broadened. When the content of B increases, the value of \(\Delta T_{ad}\) of Gd_{5.1}Si_{2}Ge_{2-x}B_{x} alloys decreases from 2.4 K for x=0.01 to 2.0 K for x=0.15.

From Fig. 5 and Table 1 it can be found that the maximum of isothermal magnetic entropy change (\(\Delta S_{ad}\)) is enlarged with Gd_{5}Si_{2}Ge_{2} compound doped by B at \(\Delta H = 1.5\) T, especially the value of \(\Delta S_{ad}\) is 13.7 J/(kg·K) for x=0.01 at \(\Delta H = 1.5\) T when Ge is replaced by B, which
Fig. 4 Curves of $M-H$ (a) and $|\Delta S_M|$ (b) of Gd$_{5.1}$Si$_2$Ge$_2$$_x$B$_x$ alloys ($x=0.01$) at $\Delta H=1.5$ T

Fig. 5 Magnetic entropy change $\Delta S_M(T, H)$ as function of temperature for Gd$_{5.1}$Si$_2$Ge$_2$$_x$B$_x$ ($x=0$, 0.01, 0.03, 0.05) at $\Delta H=1.5$ T

Table 1 Curie temperature and maximum entropy change ($\Delta S_M$) of Gd$_{5.1}$Si$_2$Ge$_2$$_x$B$_x$

| $x$  | $T_c$/K | $\mu H$/T | $|\Delta S_M|_{max}$/J·kg$^{-1}$·K$^{-1}$ |
|------|---------|-----------|----------------------------------|
| 0    | 284     | 1.5       | 5.03                             |
| 0.01 | 284     | 1.5       | 13.70                            |
| 0.03 | 289     | 1.5       | 5.40                             |
| 0.05 | 291     | 1.5       | 4.60                             |
| 0.15 | 301     | 1.5       | 2.81                             |

is much higher than that of B-undoped Gd$_{5.1}$Si$_2$Ge$_2$ in the same magnetic field. But when $x=0.01$ the maximum of isothermal magnetic entropy change ($|\Delta S_M|$) becomes small, which indicates that Gd$_{5.1}$Si$_2$Ge$_2$ compound doped by reasonable content boron can improve the magnetocaloric effect of Gd$_{5.1}$Si$_2$Ge$_2$. Fig. 5 shows two peaks in B-undoped Gd$_{5.1}$Si$_2$Ge$_2$ compound, where the first peak corresponds to the first order transition of the monoclinic Gd$_{5.1}$Si$_2$Ge$_2$-type phase and the second peak corresponds to the second order transition of the orthorhombic Gd$_{5.1}$Si$_2$-type phase [9]. This is in good agreement with the DSC curve in Fig. 2.

Fig. 6 Temperature dependence on adiabatic temperature change of Gd$_{5.1}$Si$_2$Ge$_2$$_x$B$_x$ ($x=0$, 0.01, 0.03, 0.05, 0.10, 0.15) at $\Delta H=1.2$ T

When $x=0.01$, the monoclinic Gd$_{5.1}$Si$_2$Ge$_2$-type single phase occurs a first-order phase transition in alternating magnetic field, which is in good agreement with that in Fig. 2. The origin of transition is a simultaneous structural and magnetic phase transition, the crystal structure with the orthorhombic structure in the FM state changes into the monoclinic structure in the PM state under low magnetic field [11–13]. The first-order phase transition produces large $|\Delta S_M|$. But when $x>0.01$, more high temperature orthorhombic phase Gd$_{5}$Si$_4$ is inclined to second transition and leads to the small $|\Delta S_M|.$

4 Conclusions

1) B-undoped Gd$_{5.1}$Si$_2$Ge$_2$ compound crystallizes in the monoclinic Gd$_{5.1}$Si$_2$Ge$_2$-type structure with the minor orthorhombic Gd$_{5}$Si$_4$-type structure, and its $T_c$ is 285 K. With appropriate addition of B, the alloys have the monoclinic Gd$_{5.1}$Si$_2$Ge$_2$-type structure. When $x=0.15$, Gd$_{5.1}$Si$_2$Ge$_2$ compound crystallizes in the orthorhombic Gd$_{5}$Si$_4$-type structure phase.

2) When the content of B increases, $T_c$ of Gd$_{5.1}$Si$_2$Ge$_2$$_x$B$_x$ series alloys obviously increases from 285 K for $x=0.01$ to 303 K for $x=0.15$, the magnetic entropy of Gd$_{5.1}$Si$_2$Ge$_{1.99}$B$_{0.01}$ is 13.7J/(kg·K) at $\Delta H=1.5$ T,
which gives the hope of its commercial application for
magnetic refrigeration technology.

3) When the content of B increases, $T_c$ of
$Gd_{5.1}Si_2Ge_{2-x}B_x$ series alloys obviously increases. $T_c$
increases from 284 K for $x=0$ to 303 K for $x=0.15$ in
$Gd_{5.1}Si_2Ge_{2-x}B_x$ series alloys, and the span of $T_c$ reaches
18 K which broadens the refrigeration temperature range.

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