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Effect of B alloying on magnetocaloric effect of $Gd_{5.1}Si_2Ge_2$ alloy in low magnetic field

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Abstract: A series of the $Gd_{5.1}Si_2Ge_{2-x}B_x$ alloys were prepared with arc melting in purified argon atmosphere. The effect of B addition on the magnetocaloric effect of compound $Gd_5Si_2Ge_2$ 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 $Gd_5Si_2Ge_2$ 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_5Si_4-type phases appear in the matrix of monoclinic $Gd_5Si_2Ge_2$-type phase in $Gd_{5.1}Si_{2-x}Ge_2B_x$ alloys.

Key words: B-doping; $Gd_{5.1}Si_2Ge_2$; 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 refrigerating 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 $Gd_5(Si_xGe_{1-x})_4$(0.24≤x≤0.5) alloys is the most important breakthrough in the fields of magnetic refrigerating materials [6−8]. The $Gd_5(Si_xGe_{1-x})_4$ 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 $Gd_5Si_2Ge_2$ alloy, but the effect of B element on the magnetocalric effect of $Gd_5Si_2Ge_2$ 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 $Gd_{5.1}Si_2Ge_2$ was studied.

The Curie temperature (T_c) of $Gd_5Si_2Ge_2$ alloy measured in Ames Laboratory is 276 K which is lower and narrower than that of refrigeration materials. Comparing with $Gd_5Si_2Ge_2$ alloy, nonstoichiometric $Gd_{5.1}Si_2Ge_2$ alloy is more suitable as magnetic refrigeration materials. Therefore, the magnetocaloric effect of $Gd_{5.1}Si_2Ge_2$ compound doped by B was studied in this work.

2 Experimental

The $Gd_{5.1}Si_2Ge_{2-x}B_x$ (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-

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melted method under argon atmosphere in WK−II vacuum electric arc furnace with non-consumable 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 K_α 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 (T_c) and the isothermal magnetic entropy change was calculated by magnetization curves nearby T_c. The temperature corresponding to the extreme point of dm/dt dependence of the temperature curve is Curie temperature (T_c) point. The magnetic entropy change ($|\Delta S_M|$) can be numerically calculated by [7]:

$$\Delta S_M\left(\frac{T_{s+1}+T_s}{2}\right)=\frac{\sum_f (M_s-M_{s+1})_{H_f}\,\Delta H}{T_s-T_{s+1}} \quad (1)$$

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 $Gd_{5.1}Si_2Ge_{2-x}B_x$ alloy. The results prove that as-cast $Gd_{5.1}Si_2Ge_2$ alloy is crystallized as the $Gd_5Si_2Ge_2$-type monoclinic structure. Compared with the standard $Gd_5Si_2Ge_2$ PDF card, the peaks of $Gd_{5.1}Si_2Ge_2$ alloy slightly shift toward the lower angle, but still maintain the $Gd_5Si_2Ge_2$-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 $Gd_5Si_2Ge_2$-type monoclinic structure for $Gd_{5.1}Si_2Ge_2B_x$ 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_5Si_4-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 $Gd_{5.1}Si_2Ge_2$ compound without B addition, where the first sharp endothermic peak at 273 K corresponds to the first order transition of the monoclinic $Gd_5Si_2Ge_2$-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_5Si_4-type phase (the second order transition) [9]. It is reasonable to believe that the orthorhombic Gd_5Si_4-type phase exists with monoclinic $Gd_5Si_2Ge_2$-type phase in $Gd_{5.1}Si_2Ge_2$ compound without B addition, but the content of Gd_5Si_4-type phase is too

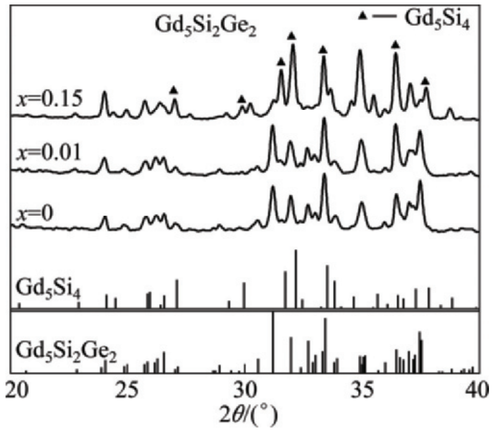

Fig. 1 XRD patterns of $Gd_{5.1}Si_2Ge_{2-x}B_x$ (x=0, 0.01, 0.15)

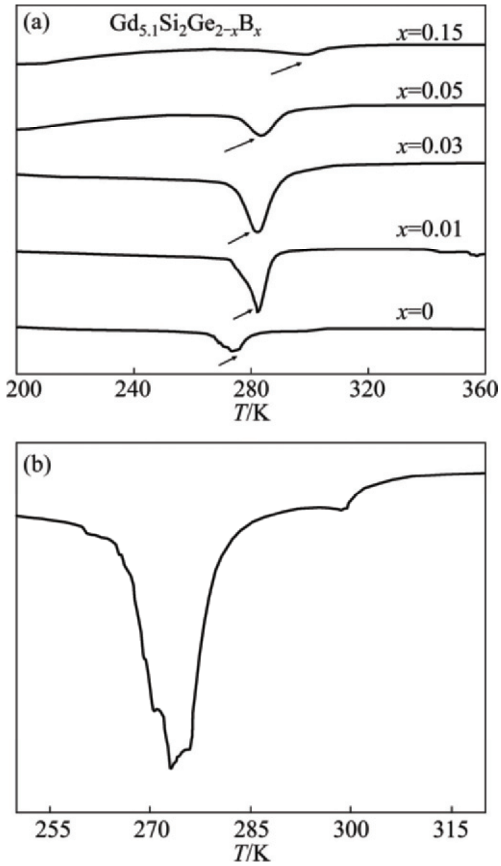

Fig. 2 DSC scans of $Gd_{5.1}Si_2Ge_{2-x}B_x$ (x=0, 0.01, 0.03, 0.15) with heating rate of 20 K/min (a) and two endothermic peaks in $Gd_5Si_2Ge_2$ compound (b)