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Influence of 1523 K annealing on phase and magnetic properties in $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds

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Abstract. **The $(Gd_{1-x}Er_x)_5Si_2Ge_2$ ($x = 0, 0{\cdot}05, 0{\cdot}1, 0{\cdot}15$ and $0{\cdot}2$) compounds were prepared from the high purity Gd metal (3 N) by arc melting, and then annealed at 1523 K (3 h). The phase, microstructure, Curie temperatures, magnetic hysteresis loss, and magnetocaloric effects were investigated. All samples retain the monoclinic $Gd_5Si_2Ge_2$ type structure. The temperature of magnetic transition decreases linearly from 281 K to 177 K with the increase of Er content from $x = 0$–$0{\cdot}2$. Because the $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds keep the typical first-order structural/magnetic transition, they display large magnetic entropy near their magnetic transition temperatures. The maximum magnetic entropy change of $(Gd_{1-x}Er_x)Si_2Ge_2$ compounds in the low magnetic field of 0∼2·0 T are 15·5, 16·1, 15·3 and 15·2 J/kg K for $x = 0{\cdot}05, 0{\cdot}1, 0{\cdot}15$ and $0{\cdot}2$, respectively.**

Keywords. **$(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds; magnetic transition; magnetic entropy change.**

1. Introduction

Since 1926, when Debye and Giauque put forward the magnetic refrigeration by magnetocaloric effect of materials (Debye 1926; Giauque 1927), the magnetic refrigeration technology progressed step-by-step. Now, it is extensively applied in microtherm field. But for a long time, the study and exploration of the room temperature refrigeration technology is almost in stagnated state. The discovery of giant magnetocaloric effect (GMCE) which is a milestone in developing room temperature magnetic refrigerant materials, in $Gd_5Si_2Ge_2$ and related $Gd_5(Si_xGe_{1-x})_4$ compounds around room temperature in 1997 made magnetic refrigerants for room temperature applications possible (Pecharsky and Gschneidner 1997a–c; Choe *et al* 2000; Morellon *et al* 2000). The giant magnetocaloric effect (GMCE) in $Gd_5Si_2Ge_2$ is attributed to a structural transition between low temperature orthorhombic phase and high temperature monoclinic phase accompanying the magnetic transition. The discovery of giant magnetocaloric effect (GMCE) in $Gd_5Si_2Ge_2$ also brought into focus the study on other $RE_5(Si_{1-x}Ge_x)_4$ (RE = Ce, Pr, Sm, Tb, Dy, Er, Ho, Y) compounds (Tegus and Dagula 2002; Yang *et al* 2003; Pecharsky *et al* 2004; Ahn *et al* 2005, 2007; Nirmala *et al* 2007a; Pereira *et al* 2008; Zhang *et al* 2009). $Tb_5Si_2Ge_2$ shows that a magnetic field induced transition occurs at about 110 K and a large MCE with the same origin as that in $Gd_5Si_2Ge_2$ is present (Zhang *et al* 2009). The Er_5Si_4 compound also has the character of the first order magnetic transition (Pecharsky *et al* 2004).

For further improving the magnetocaloric effects of $Gd_5Si_2Ge_2$ serial compounds, different rare earth elements substituted for Gd in $Gd_5(Si_xGe_{1-x})_4$ compounds have been studied. The small amount substitution of Tb for Gd in $Gd_5Si_{1.72}Ge_{2.28}$ compound decreased the Curie temperature, but the maximum magnetic entropy change in the low magnetic field change of 2·0 T for the $(Gd_{0.94}Tb_{0.06})_5Si_{1.72}Ge_{2.28}$ compound reached 25·13 J/kg K (Deng *et al* 2007). The substitutions of Dy or Y for Gd in $Gd_5Si_2Ge_2$ compound decreased the Curie temperature and the maximum magnetic entropy change (Vecchini and Moze 2004; Nirmala *et al* 2007b). The influences of Er substitution in $Gd_5(Si_xGe_{1-x})_4$ compounds has not been reported. In this work, the phase, microstructure, Curie temperatures, magnetic hysteresis loss, and magnetocaloric effects of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ ($x = 0$, $0{\cdot}05$, $0{\cdot}1$, $0{\cdot}15$ and $0{\cdot}2$) compounds were investigated.

2. Experimental

Approximately 5 g of polycrystalline $(Gd_{1-x}Er_x)_5Si_2Ge_2$ ($x = 0$, $0{\cdot}05$, $0{\cdot}1$, $0{\cdot}15$ and $0{\cdot}2$) buttons were fabricated by conventional arc melting in a high purity argon atmosphere

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using high purity Gd: 99·9 wt%, Er: 99·9 wt%, Si: 99·9999 wt% and Ge: 99·9999 wt% elements and the compounds were re-melted five times to achieve a homogeneous composition. The as-cast compound was annealed at 1523 K (3 h), in a molybdenum wire furnace of 3×10^{-3} Pa vacuum, followed by furnace cooling to room temperature. The phase purity and crystal structures were determined by powder X-ray diffraction (XRD) using Cu K_α radiation. Scanning electron microscopic (SEM) study was carried out by using Hitachi-S-3400 N. Magnetic measurements were performed using a vibrating-sample magnetometer (VSM, Lakeshore 7410). The Curie temperatures (T_C) were determined from the maxima of dM/dT of the M–T curves and were measured in an applied magnetic field of $H = 0{\cdot}02$ T. The magnetic entropy changes $\Delta S_M\,(T, H)$ were calculated from isothermal magnetization curves ($M - H$ curves) in the vicinity of the Curie temperature using the thermodynamic Maxwell relation according to (1) (Hashimoto *et al* 1981). The isothermal magnetization curves were measured in a temperature range of 150–300 K, and in magnetic fields up to 2 T.

$$\Delta S_M\,(T,\ H) \quad = \quad \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H. \tag{1}$$

3. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of the five samples collected at room temperature. By analysing and indexing the X-ray diffraction patterns of samples, one can find that all samples almost retain the monoclinic $Gd_5Si_2Ge_2$ structure. It indicates Er can substitute for Gd to form substitutional solid solutions in $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds with $x \leq 0{\cdot}2$. The main diffraction peaks of the $Gd_5Si_2Ge_2$ structure phase have obvious shift to high angle with increase in the content of Er. This is a signature of lattice contraction, which attributes to the radius of Er (1·67 Å) which is smaller than that of Gd (1·72 Å). Figure 2 shows SEM micrographs of the $(Gd_{1-x}Er_x)_5Si_2Ge_2$ samples. The character of column cellular grains and the cellular walls are very clear. The microstructure mainly composed of two parts: gray matrix basic phase and column cellular, and only very small amount of impurity phase has been detected. In addition, there are some fine lines in columnar dominant phases.

Figure 3 displays the temperature dependence on magnetization of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds with $0 \leq x \leq 0{\cdot}2$ measured under a magnetic field of 0·02 T in heating process. The Curie temperatures (T_C) can be obtained by the maximum points in the first derivative of the M–T curves for each sample. From theory, the T_C is mainly determined by the exchange interactions between the magnetic atoms. In $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds, Si and Ge are nonmagnetic, the Curie temperature is determined by the Gd–Gd, Gd–Er, and Er–Er interactions. The T_C of $Gd_5Si_2Ge_2$ compound is 281 K in this work, which is higher than 276 K of $Gd_5Si_2Ge_2$ compound reported elsewhere (Pecharsky and Gschneidner 1997a). It may be due to the purity of

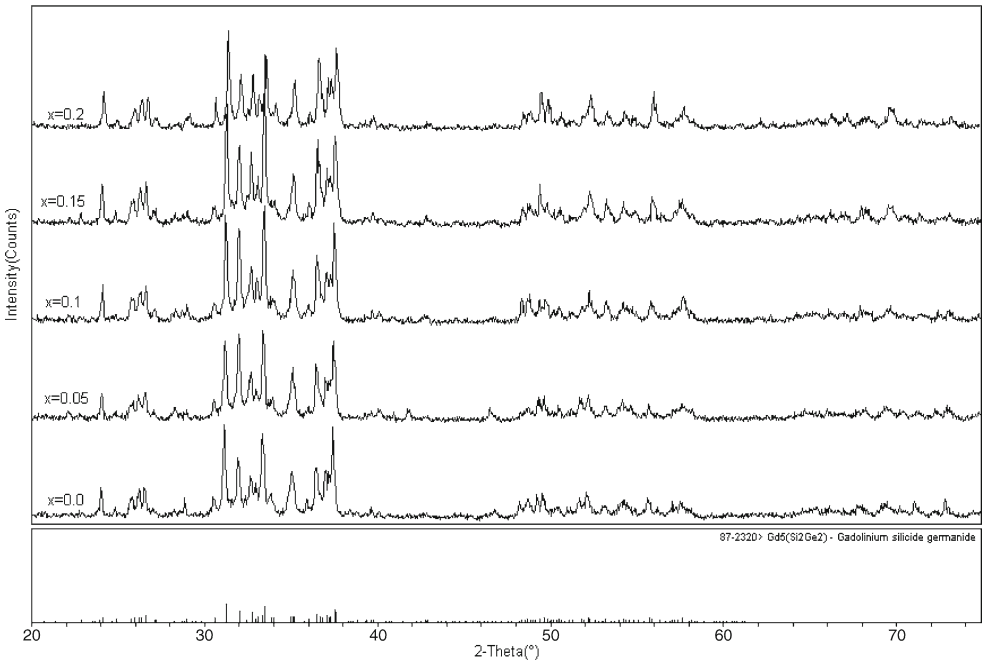

Figure 1. XRD pattern of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds.

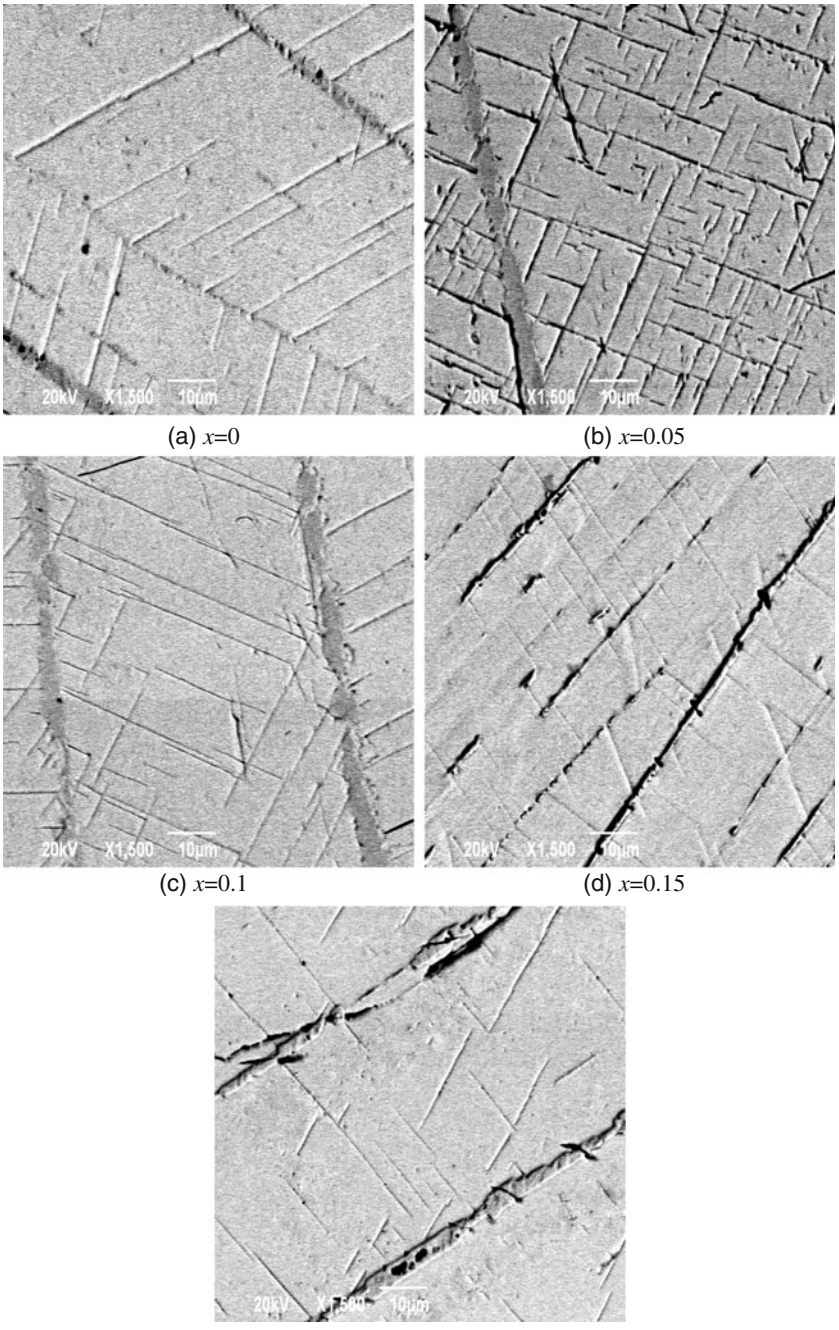

Figure 2. Backscattered SEM micrographs of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds.

starting material of Gd metal (purities better than 99·9%). But it is lower than the 300 K of that prepared from the high purity Gd metal (4 N) by arc melting, and then annealed at 1573 K (1 h) (Podmiljšak *et al* 2009). In addition, there is a unconspicuous magnetic phase transition at about 299 K in the M–T curve for $Gd_5Si_2Ge_2$ compound which indicates that the sample contains small amount of Gd_5Si_4-type phase whose T_C is at about 299 K. From table 1, one can find that the T_C of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds is very sensitive to the Er content, it decreases from 281 K to 177 K along with increasing Er content from $x = 0$ to 0·2 in the $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds. The decrease of T_C and the increase in Er content almost present linear relation, as shown in figure 4. The decrease of the Curie

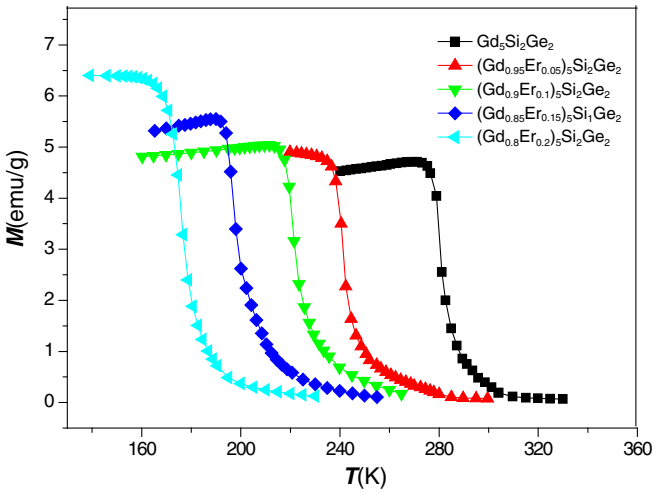

Figure 3. Temperature dependent magnetization of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds measured under 0·02 T.

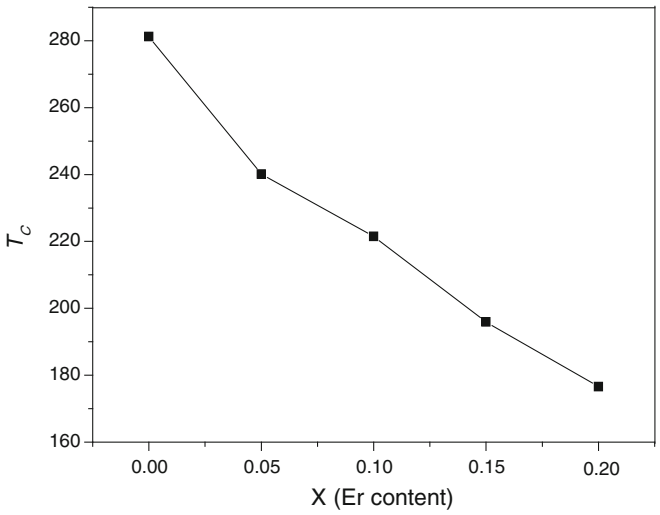

Figure 4. Details of T_C of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ dependent Er content.

Table 1. Er content, Curie temperature, maximum magnetic entropy change, and magnetic hysteresis loss of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds.

x	T_C	Maximum magnetic entropy change	Magnetic hysteresis
0·0	281·2	14·8	28·43
0·05	240·1	15·5	31·67
0·1	221·5	16·1	31·53
0·15	195·9	15·3	27·85
0·2	176·6	15·2	27·79

temperature in the Er-substituted compound is probably associated with the fact that the Gd–Gd and Gd–Er interactions are much stronger than those of the Er–Er ones in metal systems. For example, the $GdCo_2$ compound is ferromagnetic with a high Curie temperature of 405 K (Gu *et al* 2007), the T_C of $Gd_{0·6}Er_{0·4}Co_2$ is 296 K (Liu and Altounian 2005), but the $ErCo_2$ with a low Curie temperature of 33 K (de Oliveira and von Ranke 2003). In addition, the lattice contraction and the Gd–Gd interactions reduce with the increase of Er content and are also the factor of decrease of T_C.

The isothermal magnetization curves of different temperatures near the vicinity of the Curie temperature in a field of 0–2 T are shown in figure 5 (a–e). The measurements were performed in field increasing process. In order to check whether the isothermal magnetization process involves magnetic hysteresis, one of M–H curves of the samples were measured during up and down magnetic field near T_C. The M–H curves below T_C exhibit a characteristic ferromagnetic behaviour. In the temperature range of 3 K above T_C, there is a field-induced metamagnetic transition from the paramagnetic state to the ferromagnetic state, which is characterized by a step sharp change in the magnetization. The field-induced metamagnetic transition disappears in the samples with higher temperatures. The magnetic hysteresis happens inevitably in materials with a first-order phase transition, and the value of magnetic hysteretic loss is also responsive to the first-order magnetic transition intensity. A large magnetic hysteresis occurs in $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds, the maximum value is about 30 J/kg appearing at near T_C, as shown in figure 5. It indicates that the field-induced first-order transition from paramagnetic to ferromagnetic state is not weakened by introducing Er in $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds. Figure 6 shows the compared Arrott plots for the samples. According to the I–S model (Fujita *et al* 1999), negative slopes in Arrott plot curve often indicate the first order transition, and the linear relation in Arrott plot above T_C implies that the second-order magnetic transition occurs. One can find that negative slopes appear in five samples. It also means that the $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds keep the first-order structural/magnetic transition.

Magnetic entropy change, ΔS_M (T, H) was calculated by using Maxwell relation based on the M–H curves. Figure 7 shows the ΔS_M (T, H) as functions of temperature for $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds. The magnetic entropy change reaches a maximum near their Curie temperatures. The maximum magnetic entropy changes of the $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds with different Er contents are given in table 1. In this work, the maximum magnetic entropy change of $Gd_5Si_2Ge_2$ compound is 14·8 J/kg K, which is in good agreement with that of $Gd_5Si_2Ge_2$ compound prepared from high purity Gd (Pecharsky and Gschneidner 1997a), and is higher than 6·5 J/kg K and

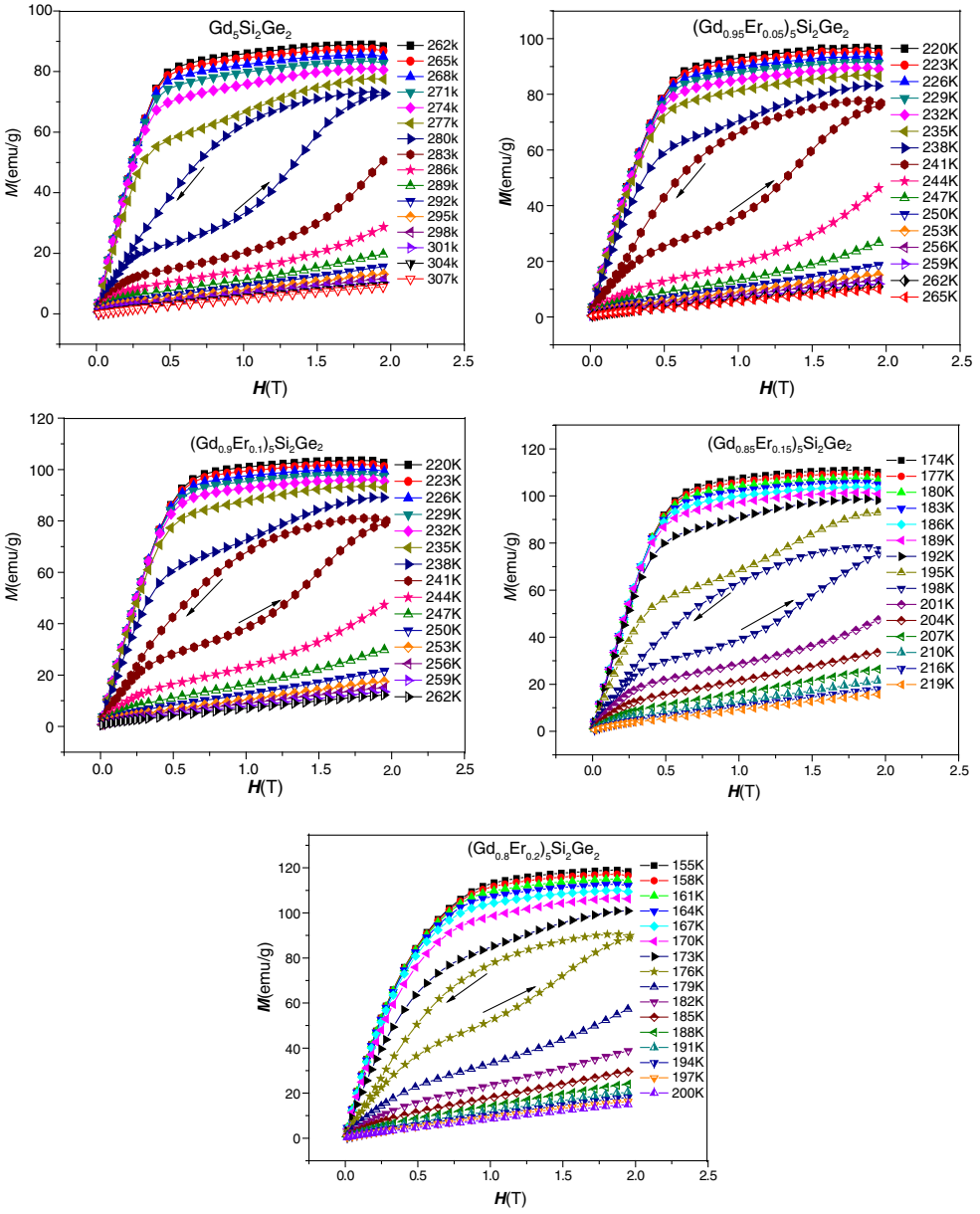

Figure 5. Magnetization isotherm curves of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds measured under field of 0–2 T: (**a**) $x = 0$, (**b**) $x = 0{\cdot}05$, (**c**) $x = 0{\cdot}1$, (**d**) $x = 0{\cdot}15$ and (**e**) $x = 0{\cdot}2$.

7·0 J/kg K of $Gd_5Si_2Ge_2$ compounds prepared from Gd metal (3 N) under magnetic field change of 0–2 T (Raj Kumar *et al* 2008, 2009). It shows that the heat treatment process in this work is beneficial to offset the disadvantage rooting from the low purity starting material of Gd metal. The maximum magnetic entropy change in the samples of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds are 15·5, 16·1, 15·3 and 15·2 J/kg K with $x = 0{\cdot}05$, 0·1, 0·15 and 0·2 in the magnetic field change of 0∼2·0 T, respectively and are larger than that of pure $Gd_5Si_2Ge_2$ compound (14·8 J/kg K) in this work.

4. Conclusions

The $(Gd_{1-x}Er_x)_5Si_2Ge_2$ ($x = 0, 0{\cdot}05, 0{\cdot}1, 0{\cdot}15$ and 0·2) compounds with the starting material of Gd metal (3 N) were prepared by arc melting, and then annealed at 1523 K for 3 h. The compounds retain monoclinic $Gd_5Si_2Ge_2$ type structure. The microstructures of five samples have the character of column cellular grains, and there are some fine lines in columnar dominant phase in all of them. With the increase in Er content, the T_C shows linear decrease from 281 K to 177 K. The compounds keep the typical first-order structural/magnetic

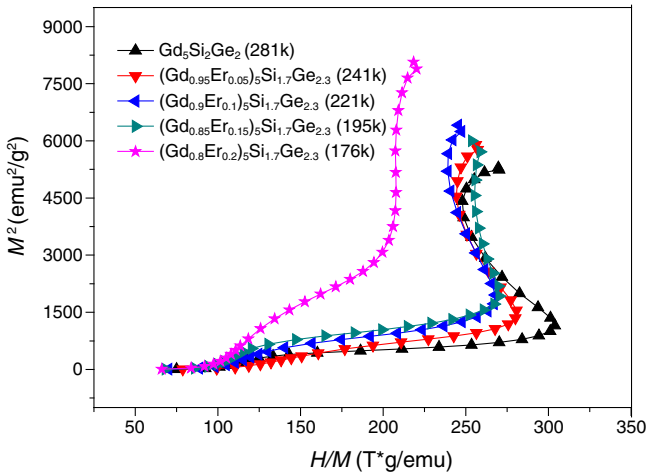

Figure 6. Arrott plots of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds.

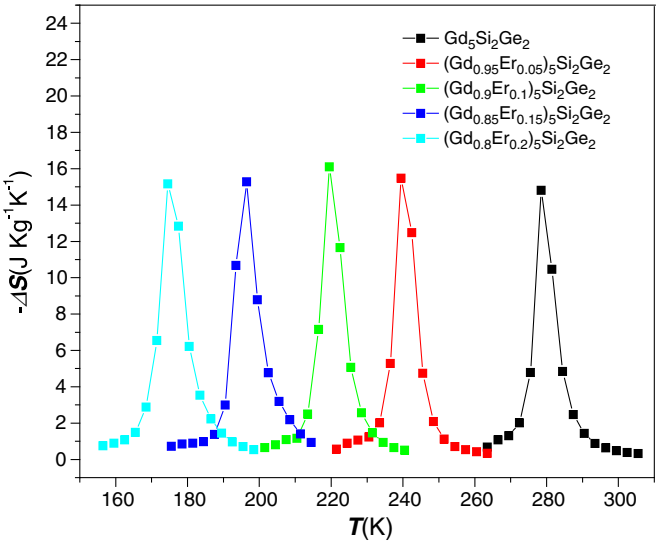

Figure 7. Magnetic entropy change ΔS_M (T, H) as functions of temperature of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ compounds.

transition and giant MCE. The maximum magnetic entropy change in the samples of $(Gd_{1-x}Er_x)_5Si_2Ge_2$ were 15·5, 16·1, 15·3 and 15·2 J/kg K with $x = 0{\cdot}05$, 0·1, 0·15 and 0·2 in the applied magnetic field change of 0∼2·0 T, respectively and are larger than that of pure $Gd_5Si_2Ge_2$ compound (14·8 J/kg K) in this work. The analysis of X-ray, the character of microstructure, and the giant MCE of samples show that the heat treatment process in this work is beneficial to offset the disadvantage rooting from the low purity starting material of Gd metal.

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