



Structural, Magnetic and Magnetocaloric Effect of $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ Compounds

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Received: 24 August 2018 / Accepted: 2 February 2019 / Published online: 19 February 2019
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Abstract

The influences of Mn/Fe ratio on the structural, magnetic and magnetocaloric properties of $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ ($x = 0.0–0.5$) compounds have been investigated by means of X-ray diffraction (XRD) and magnetic measurements. The XRD results show the compounds crystallize in the cubic $\text{Th}_6\text{Mn}_{23}$ -type structure, and the lattice size decreases with the decrease in Mn/Fe ratio. Magnetic measurements show that the samples exhibit a second-order magnetic transition from $T_C = 99$ K for $x = 0.3$ down to $T_C = 89$ K for $x = 0.4$ and increase to 293 K for $x = 0.5$. The magnetization measured at 10 K decreases from 119 emu/g for $x = 0.0$ to 82 emu/g for $x = 0.4$, but the magnetization is 105 emu/g at $x = 0.5$. For an applied field from 0 to 5 T, the maximum values of magnetic entropy change ($-\Delta S_M$) for $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ compounds with $x = 0.3, 0.4$ and 0.5 are 3.56 J/kg K, 3.77 J/kg K and 1.79 J/kg K, respectively. The properties of $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ compounds help to understand the exceptional physical characteristics and provide the information for seeking giant magnetocaloric materials.

Keywords $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ compounds · Magnetic transition · Magnetocaloric effect

1 Introduction

In recent years, rare-earth (R)–transition metal (T) intermetallic compounds of the R_xT_y type have been extensively studied due to the R–T exchange coupling interaction, which is always ferromagnetic when R is a light rare earth and antiferromagnetic with the heavy rare earths [1, 2]. Depending on the constituent element or composition, various

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properties such as magnetovolume effect [3], magnetocrystalline anisotropy [4, 5], magnetic-field-induced martensitic transformation, strain effect [6], magnetoresistance effect [7, 8] and magnetocaloric effect [9, 10] were observed. Among them, the binary R_6Mn_{23} compounds crystallize in the Th_6Mn_{23} -type structure (space group $Fm\bar{3}m$), which comprises one crystallographic site for the R atoms (24e) and four sites for the Mn atoms (4b, 24d, $32f_1$ and $32f_2$) [11–13]. And, the magnetic transition temperature of R_6Mn_{23} compounds is at high Curie temperature ($T_C=400\text{--}500$ K) [14–17]. In addition, among the binary Gd–Mn systems, Gd_6Mn_{23} compound ($T_C\sim 500$ K) is believed to violate this antiferromagnetic coupling for a long time, which is because the magnetization of Gd_6Mn_{23} is larger than that of Y_6Mn_{23} [1, 18–21], and the magnetization of R_6Mn_{23} involves a heavy rare-earth element [20]. Neutron diffraction experiments [21] had also confirmed that the Gd–Mn coupling was antiferromagnetic in fact, as always observed. More recently, the magnetocaloric properties of the Th_6Mn_{23} -type R_6Mn_{23} compounds were systematically studied [22], including their derivatives $Gd_{6-x}R_xMn_{23}$ [23], $Gd_6(Mn_{1-x}Co_x)_{23}$ ($x\leq 0.3$) [24] and $Gd_6(Mn_{1-x}Fe_x)_{23}$ ($x\leq 0.2$) [25]. In these ferromagnetic materials, the R and T ($T=Mn$ or Fe) sublattices order magnetically at two different temperatures which can be altered by chemical replacement. For example, Fe substitution can effectively reduce the ordering temperature from $T_C=489$ K for $x=0.0$ to $T_C=176$ K for $x=0.2$ in $Gd_6(Mn_{1-x}Fe_x)_{23}$ [25]. Similar results were found in Co-substituted $Gd_6(Mn_{1-x}Co_x)_{23}$ system [24].

In this work, based on the research results of references [22–25] and our related research on Gd–Fe–Mn system [26], we have to further focus on the influences of the Mn/Fe ratio on magnetic and magnetocaloric properties of the $Gd_6(Mn_{1-x}Fe_x)_{23}$ ($x=0.3, 0.4, 0.5$) compounds, which expand the Fe composition range. This work helps to further understand the physical properties of Gd_6Mn_{23} system and to explore their potential value for future cooling applications.

2 Experiment

Polycrystalline $Gd_6(Mn_{1-x}Fe_x)_{23}$ ($x=0.0\text{--}0.5$) samples were synthesized by arc melting technique using stoichiometric amounts of Gd (99.99%), Mn (99.99%) and Fe (99.99%) under a purified argon atmosphere. To ensure homogeneity, the ingots were re-melted three times. Then, the samples are wrapped in tantalum foils, sealed in a high-vacuum quartz tube, annealed at 800°C for 5 days and finally quenched in ice water. The crystal structure was studied using powder X-ray diffraction (XRD) patterns with a $Cu\ K\alpha_1$ radiation experiment at room temperature. Magnetization measurements were taken in the temperature range from 10 to 380 K with an external applied magnetic field up to 50 kOe using a physical property measurement system (PPMS-9, Quantum Design.)

3 Results and Discussion

Figure 1 shows the XRD patterns measured at room temperature and Rietveld refinement results of $Gd_6(Mn_{1-x}Fe_x)_{23}$ ($x=0.0\text{--}0.5$) compounds. In order to reveal the crystal structure, the XRD patterns were analyzed using FullProf package. The

Fig. 1 Rietveld refined powder XRD patterns of $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ ($x=0.0-0.5$) compounds (Color figure online)

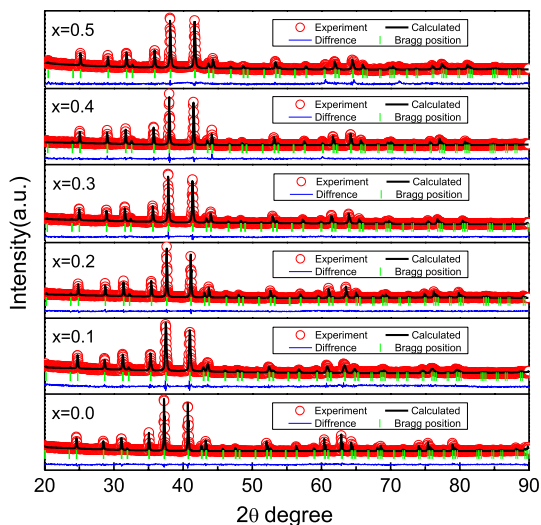
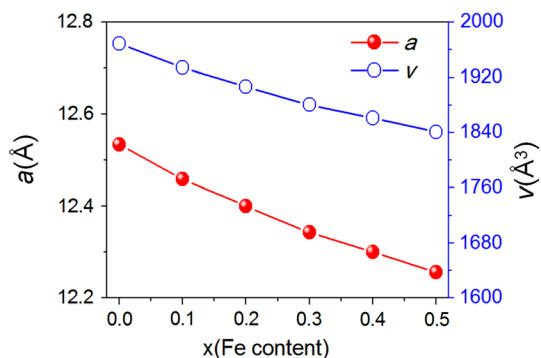


Fig. 2 Lattice constants a and the unit-cell V values of $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ as a function of Fe content x (Color figure online)



original record data are indicated by red circles, and the calculated profile is the continuous line overlying them. The lower curve shows the difference between the observed and calculated intensity. The detailed analysis of the results confirms that all samples exist as a single cubic phase with the $\text{Th}_6\text{Mn}_{23}$ -type structure (space group of $\text{Fm}\bar{3}\text{m}$) and form a continuous solid solution [18–25]. The values of the lattice constants derived through the Rietveld refinement are presented as a function of Fe concentration x in Fig. 2, and the values are listed in Table 1. The R-values and GOF of these refinements consequences are also given in Table 1, suggesting that these results agree well with those reported for $\text{Gd}_6\text{Mn}_{23}$ alloys [12, 13, 18–25]. As is well known, the displacement of foreign atoms with distinct radii can lead to changes in lattice parameters. In this compound, the lattice dimensions decrease almost linearly with the Fe content, owing to the smaller metallic radius of Fe compared to that of Mn.

The magnetization as a function of temperature ($M(T)$) for $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ ($x=0.3, 0.4, 0.5$) compounds is measured in the 200 Oe external field from 10 to

Table 1 The lattice constants a , unit-cell volume V , GOF and T_C of $Gd_6(Mn_{1-x}Fe_x)_{23}$ compounds

Compound	a (Å)	V (Å ³)	GOF	R_{wp} (%)	R_{exp} (%)	$T_C \pm 5$ (K)	Remarks
Gd_6Mn_{23}	12.534(2)	1969.21(0)	3.6	14.6	7.2	489 [18–25]	This work
$Gd_6(Mn_{0.9}Fe_{0.1})_{23}$	12.458(9)	1933.93(8)	2.4	11.4	8.1	369 [18, 19, 25]	This work
$Gd_6(Mn_{0.8}Fe_{0.2})_{23}$	12.400(0)	1906.62(8)	1.7	13.6	9.8	176 [18, 19, 25]	This work
$Gd_6(Mn_{0.7}Fe_{0.3})_{23}$	12.342(8)	1880.34(0)	3.7	14.2	7.6	99	This work
$Gd_6(Mn_{0.6}Fe_{0.4})_{23}$	12.300(6)	1861.14(3)	1.6	10.3	9.7	89	This work
$Gd_6(Mn_{0.5}Fe_{0.5})_{23}$	12.256(5)	1841.17(1)	2.1	12.6	8.5	293	This work

380 K on heating process, as shown in Fig. 3a. The results show that the magnetization decreases rapidly with the increase in temperature, suggesting the occurrence of a magnetic phase transition from ferromagnetic to paramagnetic state. Here, T_C is defined as the temperature where dM/dT is the minimum. It has been previously reported that the T_C of Gd_6Mn_{23} compounds is 489 K [18–25]. As shown in the inset of Fig. 3a, the T_C of the compound changes with the Fe content.

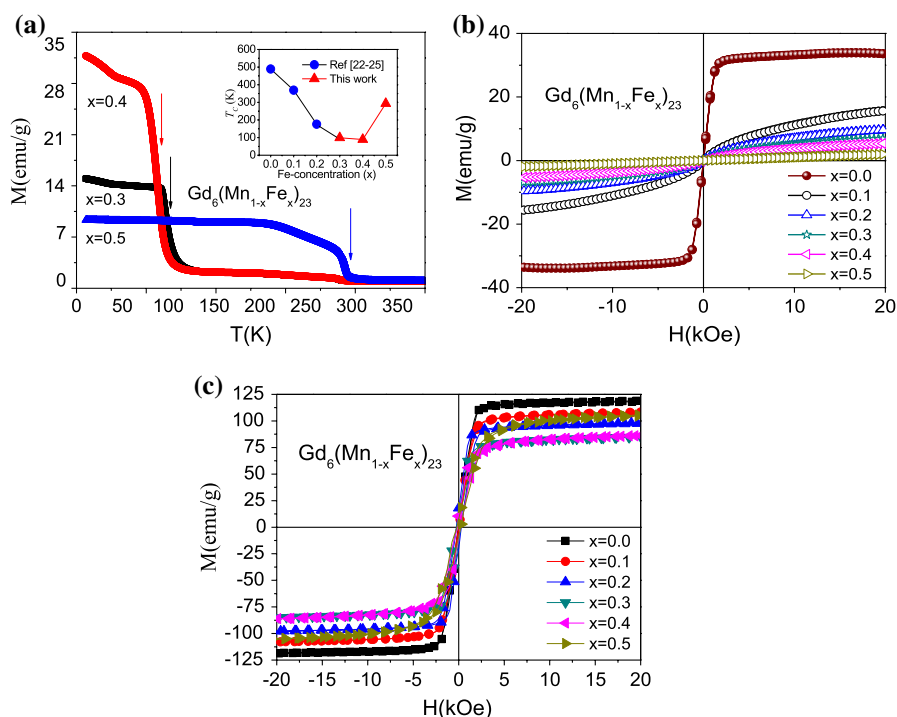


Fig. 3 Temperature dependence of magnetization for $Gd_6(Mn_{1-x}Fe_x)_{23}$ ($x=0.3, 0.4, 0.5$) compounds on heating in the field of 200 Oe (a); the inset shows the T_C of $Gd_6(Mn_{1-x}Fe_x)_{23}$ as a function of Fe content x . Magnetization curves for the $Gd_6(Mn_{1-x}Fe_x)_{23}$ compounds measured at 300 K (b) and magnetization curves for the $Gd_6(Mn_{1-x}Fe_x)_{23}$ compounds measured at 10 K (c) (Color figure online)

From Ref. [25], the T_C is 369 K at $x=0.1$ and 176 K at $x=0.2$. In this work, the T_C at $x=0.3, 0.4$ and 0.5 is 99 K, 89 K and 293 K, respectively. As is well known, the structural and magnetic properties of these compounds are strongly dependent on their composition [15, 16, 18–28]. Therefore, three reasons can account for the drastic change in T_C when the x increases from 0.0 to 0.4: (i) It is recognized that the substitution of foreign atoms with different radii, which can be treated as ‘chemical pressure,’ may possess an effect similar to applying external mechanical pressure [29]. Since the radius of Fe ions is smaller than that of Mn, the substitution of Fe for Mn can induce the contraction of lattice in $Gd_6(Mn_{1-x}Fe_x)_{23}$ compounds and consequently modify the relative stability between the ferromagnetic and paramagnetic state, leading to the decrease in T_C . (ii) The substitution of Fe for Mn would enhance the antiferromagnetic coupling interactions between Mn and Fe in $Gd_6(Mn_{1-x}Fe_x)_{23}$ compounds and take the responsibility of decreasing T_C to some extent [1, 2, 15, 16, 19, 22–25]. (iii) In R_6Mn_{23} compounds involving a heavy rare-earth element, the R magnetic moments couple antiferromagnetically with the Mn sublattices to form complex non-collinear magnetic structures [21, 30]. The (usual) negative sign of the Gd–Mn magnetic exchange has been confirmed by neutron inelastic scattering on Gd_6Mn_{23} [31]. The decrease in both the magnetization and the ordering temperature upon Fe substitution in $Gd_6(Mn_{1-x}Fe_x)_{23}$ is due to the Fe atoms carrying a lower magnetic moment than that of Mn atoms in these phases [25]. Interestingly, the T_C suddenly increases to 293 K at $x=0.5$. The ratio of Fe/Mn = 1:1 is probably a critical value in the system of $Gd_6(Mn_{1-x}Fe_x)_{23}$. When the iron concentration reaches the critical value, the exchange coupling between Fe and Gd is stronger than that between Gd and Mn. Furthermore, the ferromagnetic coupling between Gd and Fe needs a higher temperature to break the Gd and Fe interaction. For this reason, the magnetic transition temperature increases to 293 K at $x=0.5$. In order to know the effect of Fe content on magnetic moment of $Gd_6(Mn_{1-x}Fe_x)_{23}$ compounds, magnetic hysteresis loops were investigated at 10 K, as shown in Fig. 3c. It can be seen that the magnetization decreases from 119 emu/g ($x=0.0$) to 82 emu/g ($x=0.4$), which owns to antiparallel coupling of the magnetic moment between Mn and Fe atoms. However, the magnetization increases to 105 emu/g at $x=0.5$. As mentioned above, the strong coupling between Gd and Mn at the critical value occurs in the system, so the overall moment increases to a higher value. And, more remarkable, the $Gd_6(Mn_{1-x}Fe_x)_{23}$ compounds possess very minor magnetic hysteresis loss at room temperature, which is beneficial to the improvement in magnetic refrigeration efficiency.

The isothermal magnetization (M – H) curves were measured in a magnetic field up to 50 kOe in the vicinity of T_C . When one curve is finished, the magnetic field is reduced to zero isothermally and slowly, and then, the temperature is increased for the next $M(H)$ curve. The temperature was changed in steps of 2 K in the vicinity of T_C and in steps of 5 or 10 K far from T_C . The field sweeping rate is slow enough to ensure that data are recorded in an isothermal process. Figure 4a, b shows the magnetization isotherms of $Gd_6(Mn_{1-x}Fe_x)_{23}$ compounds for $x=0.3, 0.4$ and 0.5 , respectively. Obviously, a typical ferromagnetic transition is evident near T_C . Based on M – H curves, the

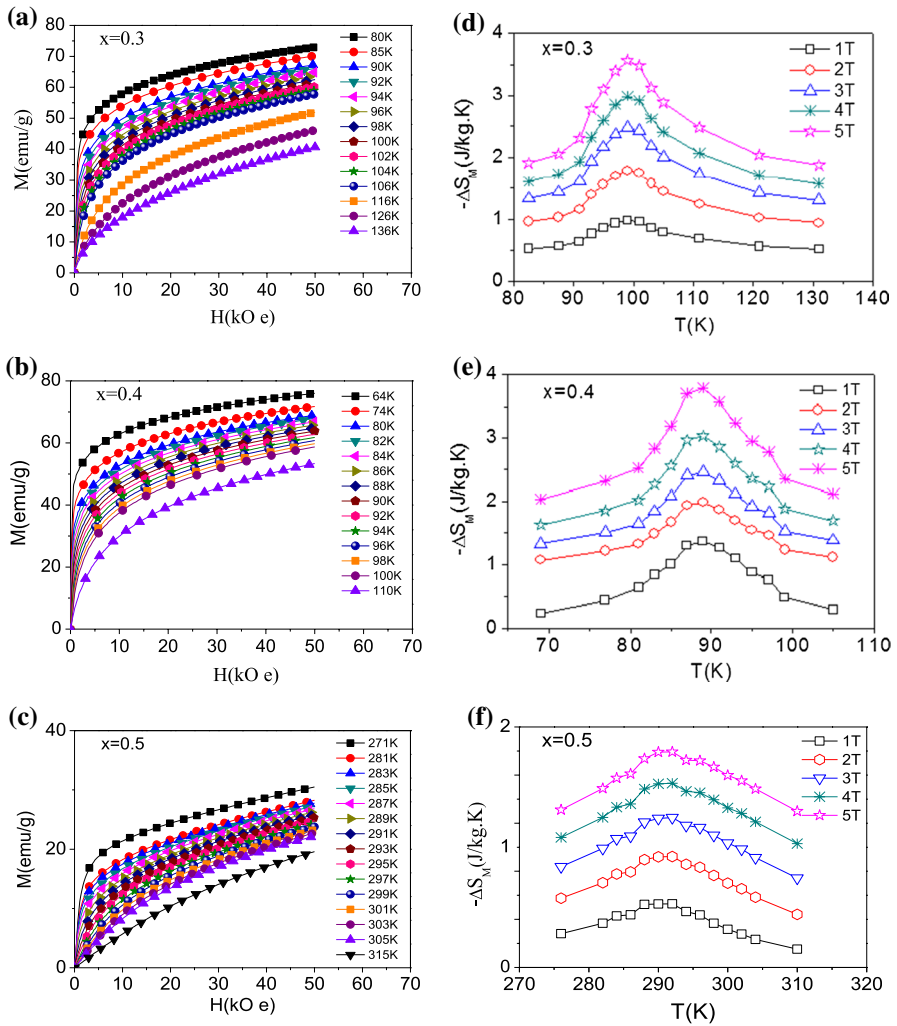


Fig. 4 The isothermal magnetization curves for $Gd_6(Mn_{1-x}Fe_x)_{23}$ ($x=0.3, 0.4, 0.5$) compounds, measured in the vicinity of T_C (a–c). Temperature dependence of $-\Delta S_M$ for $Gd_6(Mn_{1-x}Fe_x)_{23}$ ($x=0.3, 0.4, 0.5$) compounds at T_C (d–f) (Color figure online)

magnetic entropy change (ΔS_M) for a magnetic field change from 0 to 50 kOe was calculated by using the Maxwell relation [32]:

$$\Delta S_M(T, \Delta H) = \int_0^H \left(\frac{\partial M(H, T)}{\partial T} \right)_H dH$$

Figure 4d–f shows ΔS_M – T curves in the field of 0–5 T for $Gd_6(Mn_{1-x}Fe_x)_{23}$ ($x=0.3, 0.4, 0.5$) compounds. As expected, the maximum ΔS_M was observed at the transition temperatures. ΔS_M increases obviously with the increase in applied magnetic field.

The maximum of $|\Delta S_M|$ for a field change of 0–5 T increases slightly from 3.56 to 3.77 J/kg K with x increasing from 0.3 to 0.4, but reduces to 1.79 J/kg K at $x=0.5$. The refrigerant capacity or relative cooling power (RCP) is another important quality factor of the refrigerant materials which is a measurement criterion of heat transfer between the cold and hot reservoirs in an ideal refrigeration cycle. In this work, on the basis of Gschneidner and Pecharsky [33], the RCP value is defined as $RCP = -\Delta S_M \times \delta T_{FWHM}$ based on the ΔS_M-T curve, where δT_{FWHM} is the full width at half maximum. The RCP values of $Gd_6(Mn_{1-x}Fe_x)_{23}$ ($x=0.3, 0.4, 0.5$) are 44.04, 51.56 J/kg and 108 J/kg for an applied field change of 0–5 T.

A conventional and most straightforward method to identify the nature of a phase transition is the Banerjee criterion based on an Arrott plot [34]. It is generally agreed that a negative slope or presence of an inflection point in the Arrott plot is related to a first-order magnetic phase transition (FOMT), while a positive slope or linear behavior near T_C indicates a second-order magnetic phase transition (SOMT). Figure 5a–c shows Arrott plots of three samples, which show curves of M^2 versus H/M near the T_C . For the $Gd_6(Mn_{1-x}Fe_x)_{23}$ ($x=0.3, 0.4, 0.5$) compounds, the absence of a negative slope and an inflection point indicates a SOMT behavior. Generally, most magnetic transitions are of second order and the materials with second-order magnetic phase transitions exhibit very small magnetocaloric effect than the materials with first-order magnetic phase transitions [35–37].

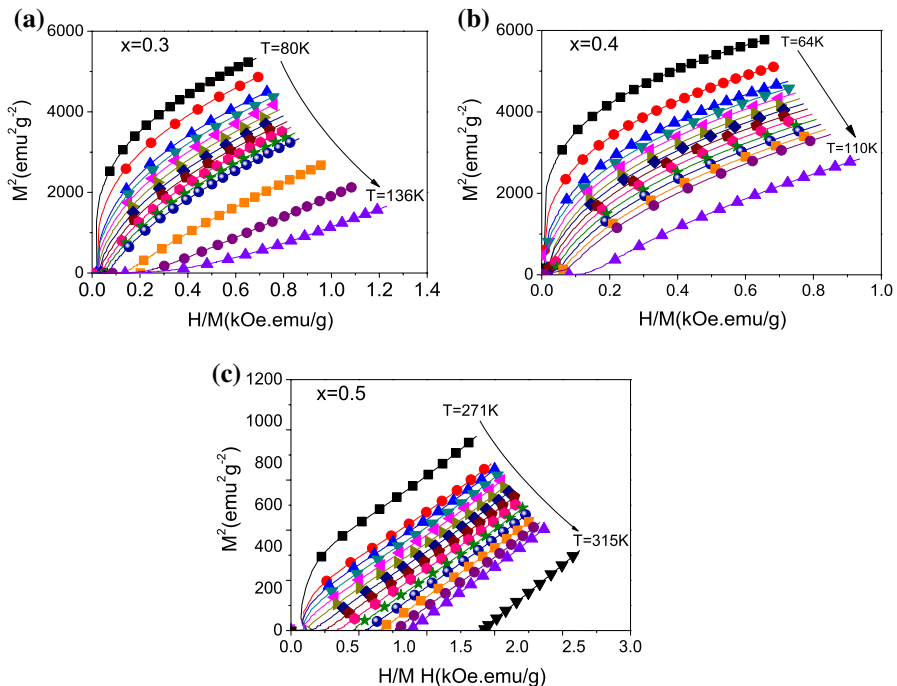


Fig. 5 Arrott plots for the $Gd_6(Mn_{1-x}Fe_x)_{23}$ compounds with **a** $x=0.3$; **b** $x=0.4$ and **c** $x=0.5$ (Color figure online)

4 Conclusions

The $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$ compounds ($x=0.0-0.5$) have been synthesized and studied. The results show that the samples are a single phase, crystallizing in the cubic $\text{Th}_6\text{Mn}_{23}$ -type structure. With a decrease in the Mn/Fe ratio, the lattice parameter a and unit-cell volume V decrease. From $x=0.0$ to $x=0.4$, the T_C moves to lower temperatures, but increases to 293 K at $x=0.5$. The magnetization of all compounds at 300 K decreases to the Fe substitution up to $x=0.5$, which is lower than that at 10 K. The type of magnetic phase transition from ferromagnetic to paramagnetic is second order, the maximum values of $|\Delta S_M|$ and RCP for a magnetic field change of 0–5 T for $x=0.3$, $x=0.4$ and $x=0.5$ are 3.56, 3.77 J/kg K and 1.79 J/kg K and 44.04, 51.56 J/kg and 108 J/kg, respectively. The present results may give some clue for searching new magnetocaloric materials with large MCE.

Acknowledgements This work is supported by the National Natural Science Foundation of China (51461012, 51761007), the Guangxi Key Laboratory of Information Materials (171017-Z, 171022-Z), the Guangxi Natural Science Foundation (2016GXNSFAA380030, 2016GXNSFGA380001), GUET Excellent Graduate Thesis Program (16YJPYSS32) and Innovation Project of GUET Graduate Education (2018YJXC84).

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