Giant magnetocaloric effect in $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ compounds*

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The crystal structure, magnetic and magnetocaloric characteristics of the pseduo ternary compounds of $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($0 \leq 2x \leq 0.1$) were investigated by x-ray powder diffraction and magnetization measurements. The x-ray powder diffraction results show that all compounds preserve the monoclinic phase as the majority phase and all the synthesized compounds were observed to be ferromagnetic from magnetization measurements. Magnetic phase transitions were interpreted in terms of Landau theory. Maximum isothermal magnetic entropy change value ($20.84\ J \cdot kg^{-1} \cdot K^{-1}$) was found for $Tb_5Ge_{1.95}Si_{1.95}Mn_{0.1}$ at around 123 K in the magnetic field change of 5 T.

Keywords: magnetic properties, magnetocaloric effect, isothermal magnetic entropy change
PACC: 7530S, 7550C

1. Introduction

The term magnetocaloric effect (MCE) refers to a reversible change of temperature resulting from a change in the magnetization of a magnetic material, which was first observed by Warburg in 1881 on samples of iron.[1] In a material displaying MCE, the alignment of randomly oriented magnetic moments by an external magnetic field results in heating of the material. If the magnetic field is subsequently turned off, the magnetic moments randomize again, which leads to cooling of the material.

Over the years, study of MCE in magnetic material has developed into an efficient tool to understand the correlations between magnetic, structural and thermal properties. Recent studies on the MCE of various materials affirm that a high value of MCE is the most important requirement for the use of the material in magnetic refrigeration applications.

MCE of $Gd_5(Si,Ge)_4$,[2] MnFe(P,As,Ge)[3] and H-treated $La(Fe,Si)_{13}$[4] have been extensively studied due to their potential use for magnetic refrigeration applications. These compounds undergo a first-order phase transition and exhibit large MCE. $R_5Si_2Ge_2$ compounds show interesting magnetic properties along with large MCE values with magneto-structural transition near room temperature.[5,6] A martensitic like, displacement of structural transition from an orthorhombic to a monoclinic phase (at about 276 K) occurs simultaneously with the ferromagnetic phase to paramagnetic phase transition (at about 299 K). Reverse transformations are observed with decreasing temperature. Tb is next to Gd in the periodic table of elements and has a very similar behaviour as Gd in the $Gd_5(SiGe)_4$ families with a magneto-structural transition near liquid nitrogen temperatures.[7–11] Morellon *et al.*[7] worked about magnetocaloric effect in $Tb_5Si_2Ge_2$ alloy and they have found that in an external magnetic field of 5 T a large entropy change of $21.8\ J \cdot kg^{-1} \cdot K^{-1}$ is achieved at a first-order para- to ferromagnetic transition, $T_C = 105$ K. Tegus *et al.*[9] studied the magnetic and magnetocaloric properties of the $Tb_5Si_2Ge_2$ alloy. They reported a Curie temperature T_C of 76 K, under an applied magnetic field of 0.05 T. The maximum value of magnetic entropy change that they have observed in an external magnetic field of 5 T was $19.5\ J \cdot kg^{-1} \cdot K^{-1}$.

In our previous studies on the alloying of $Tb_5Si_2Ge_2$ with Fe, Pb and Sn[12,13] we found that by Fe alloying, the first order transition is suppressed and the samples show only second order phase transitions; with no change of the Curie temperature T_C and the isothermal magnetic entropy change. The maximum entropy change, refrigerant capacity, and the relative cooling power of $Tb_5Si_{1.975}Ge_{1.975}Fe_{0.05}$ at a

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magnetic field change of 5 T was 13.28 $J \cdot kg^{-1} \cdot K^{-1}$, 461.82 $J \cdot kg^{-1}$ and 511.65 $J \cdot kg^{-1}$, respectively. The $M(H)$ measurements at temperatures around T_C show hysteresis losses for $Tb_5Si_2Ge_2$ which was not observed for the Fe alloyed samples. In the Pb and Sn alloyed compounds, the structural and magnetic phase transitions occur in a wide temperature range with respect to the parent alloy. According to the x-ray diffraction data, the unit cell parameters for Pb and Sn alloyed compounds were increased with alloying proportion as expected. As a result of this increase in the unit cell parameters the exchange interaction between magnetic atoms are reduced and consequently both the crystal structure and magnetic structure are significantly affected. It is a well-known fact that, rapid change of magnetization with temperature is a favourable property to obtain Giant MCE (GMCE). The magnetic and structural transitions of Pb and Sn alloyed compounds occur rather gently in comparison to parent alloy, thus lower magnetic entropy change values with respect to parent alloy were obtained. The maximum $|\Delta S_M|$ values observed for $Tb_5Si_{1.975}Ge_{1.975}Pb_{0.05}$ and $Tb_5Si_{1.975}Ge_{1.975}Sn_{0.05}$ were 11.27 $J \cdot kg^{-1} \cdot K^{-1}$ and 5.83 $J \cdot kg^{-1} \cdot K^{-1}$ at 5 T, respectively.

The influences of Mn that is included in the structure,[14] substitution on the phase formation, the Curie temperature, and the isothermal magnetic entropy change of the $Tb_5Si_2Ge_2$ compounds are discussed in this paper. Moreover, we also compare the results of Mn doping in $Tb_5Si_2Ge_2$ compound with our earlier studies on the doping with Fe, Pb and Sn.[12,13]

2. Experimental

Polycrystalline $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ compounds with $2x = 0$, 0.08 and 0.10 were prepared by arc-melting in argon atmosphere with Tb (99% purity), Si (99.95%), Ge (99.99%) and Mn (99.95%). The melting process was repeated five times to ensure material homogeneity. After arc-melting, the resulting ingots were sealed in quartz tubes under vacuum and annealed at 900 °C for 24 hours. The x-ray powder diffraction data of the samples were collected between 25° to 60° (2θ) at room temperature using a Rigaku D-Max 2200 diffractometer. The magnetization measurements were carried out in a Quantum Design Physical Properties Measurements System (PPMS). T_C were determined from magnetization versus temperature measurements carried out in an applied field of 5 mT. The magnetizations of the samples were first measured in the zero-field-cooled (ZFC) mode, whereby the samples were first cooled from 250 K to 5 K in the absence of magnetic field. Then, the magnetic field was applied and the temperature was increased to 250 K. Subsequently, without removing the field, field-cooled (FC) measurements were made by decreasing temperature back to 5 K. As the last step, again without removing the field, the magnetization was measured in a field-heated (FH) mode by increasing temperature. Magnetization versus magnetic field data was collected while the applied magnetic field was increasing from 0 to 5 T around the transition temperature with 5 K temperature increment steps.

The magnetocaloric effect is numerically calculated from the magnetization versus magnetic field data using the integrated Maxwell relation

$$\Delta S_M = \int_{T_1}^{T_2} \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H, \tag{1}$$

using the numerical expression:[15]

$$\Delta S_M = \frac{1}{2\delta T}\left(\delta M_1 \delta H_1 + 2\sum_{k=1}^{n-1} \delta M_k \delta H_k + \delta M_n \delta H_n\right), \tag{2}$$

where $\delta T = T_k - T_{k-1}$ is the temperature interval between two isotherms, n is the number of points that are measured for the two isotherms with the magnetic field changing by δM and δH is the difference in the magnetization from (1) to n and $T = (T_k + T_{k-1})/2$.

3. Results and discussion

3.1. Structural properties

The x-ray diffraction patterns of $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) compounds at room temperature are shown in Fig. 1.

Each phase is indicated with a different mark. The major phase of compunds is monoclinic with the space group $P\ 112_1/a$. However there are some impurity phases with orthorhombic Tb_5Si_4, hexagonal Tb_5Si_3 and hexagonal TbGe crystal structure mostly from impurities related with the rare earth element.[16] For this kind of R_5Z_4 structures (R: Rare Earth, Z: Si, Ge) the covalent bonds between Si–Si, Si–Ge and Ge–Ge atoms and the length of these bonds define the

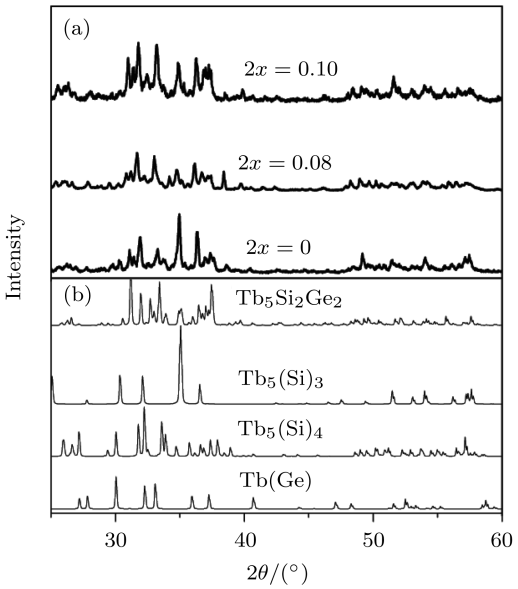


Fig. 1. The powder x-ray diffraction patterns of $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) compounds at room temperature (a) observed and (b) calculated from International Centre for Diffraction Date (ICDD) cards.

fundamental magnetic and structural properties.[17] Unit cell parameters and unit cell volume of $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) are given in Table 1. The unit cell volume decreases with the increase of Mn content.

In $R_5(SiGe)_4$ systems the magnetism of 4f states are explained by indirect Rudermann-Kittel–Kasuya–Yosida (RKKY) interactions. RKKY indirect 4f–4f interaction, which is the main magnetic exchange mechanism in 4f intermetallic compounds, is expected to be supplemented in $Tb_5Si_2Ge_2$ by direct interlayer superexchange over the Tb–(Si/Ge)(Si/Ge)–Tb bonding connecting the slabs.[17] As the Mn content is increased the Tb–(Si/Ge)(Si/Ge)–Tb bond lengths are reduced as a consequence of the decrease in unit cell volume, whence the Tb–Tb exchange interaction is increased. Unit cell volume, Tb–(Si/Ge)(Si/Ge)–Tb length and isotropic magnetic entropy change shown in Fig. 2. The results show that, there could be a linear relation between the Tb–(Si/Ge)(Si/Ge)–Tb bond lengths and the isotropic magnetic entropy change.

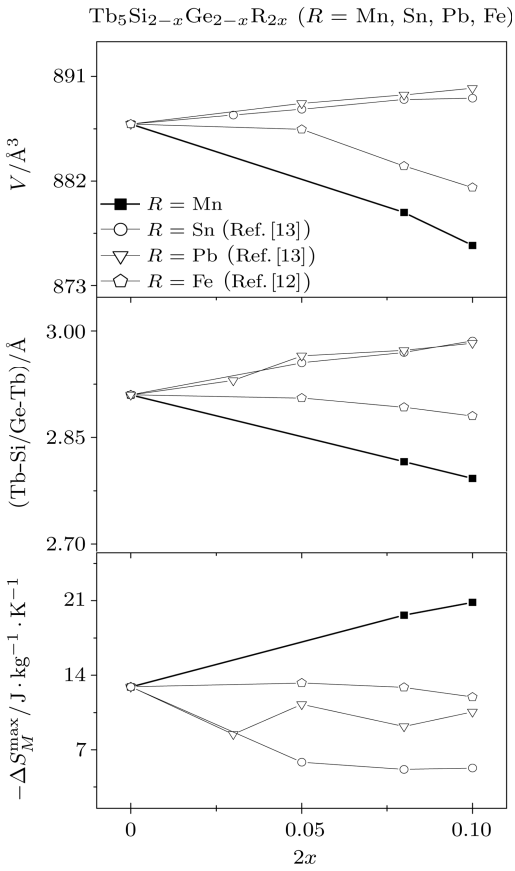


Fig. 2. The Unit cell volume, the distance between the Tb–(Si/Ge)(Si/Ge)–Tb atoms and magnetic entropy change versus $Tb_5Ge_{2-x}Si_{2-x}R_{2x}$ compounds.

Table 1. The lattice parameters and unit cell volumes of $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) compounds. (1 Å = 0.1 nm).

$2x$	a/Å	b/Å	c/Å	γ/(°)	V/Å^3
0	7.8444 (4)	14.8526 (6)	7.6234 (1)	93.0771 (2)	886.91 (2)
0.08	7.8102 (2)	14.8221 (5)	7.6004 (3)	93.0323 (2)	878.84 (3)
0.10	7.7803 (2)	14.8011 (5)	7.5843 (3)	93.0564 (3)	873.45 (2)

3.2. Magnetic properties

The results of the temperature dependent magnetization measurements $M(T)$ are given in Fig. 3. Curie temperatures (T_C) of the samples are estimated from the inflection point in $M(T)$. T_C's for all compounds are shown by vertical arrows in Fig. 3. The spin reorientation temperature (T_{sr}) is also found for all samples and given in Table 2. Both T_C and T_{sr} increase with the increase of Mn content. The values obtained for the $Tb_5Ge_{1.95}Si_{.195}Mn_{0.1}$ compound are $T_C = 123$ K and $T_{sr} = 102$ K.

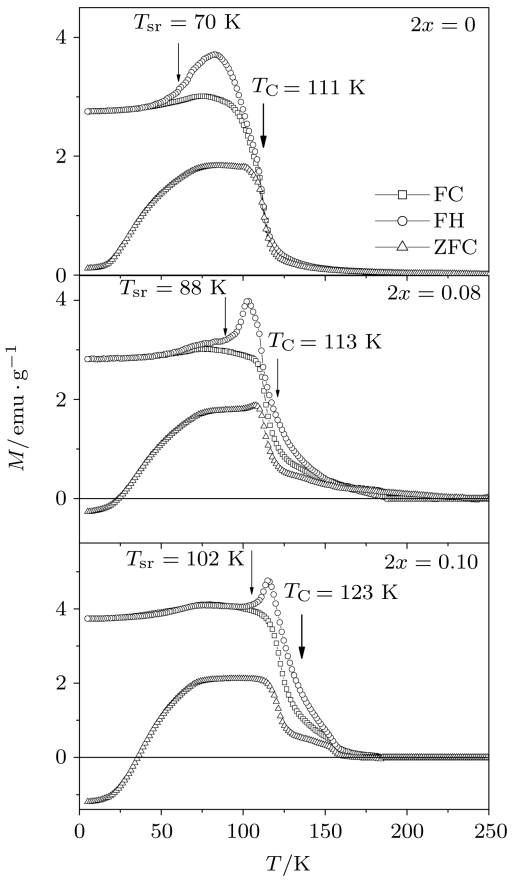


Fig. 3. The field cooled (FC), zero field cooled (ZFC), field heated (FH) curves in magnetic field of 5 mT for $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) compounds.

$M(T)$ measurements were done in the ZFC, FC and FH sequence. For all samples the ZFC and FC data separate from each other below magneto-structural transition temperature, which can be explained by wall pinning of the magnetic domains occurring in these systems.[11] FC and FH data reveals that, the more thermal hysteresis, the more Mn amount we added. This thermal hysteresis increment is of benefit to structural phase transition and besides whether the more this increase grows, the more the intensity of the structural phase transition is.[18] For instance, the thermal hysteresis of $2x = 0$ smaple is 2 K whilst it is about 7 K for $2x = 0.10$ sample. Magnetic field dependent magnetization measurement values near the transition temperatures of $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) compounds are given in Fig. 4. The magnetization values of compounds increase with the Mn content increase which is related to the increase of ferromagnetic ion density.

In order to determine the type of the magnetic transition we have drawn the Arrott plots (M^2 vs H/M) as shown in Fig. 5. The S-shaped (negative

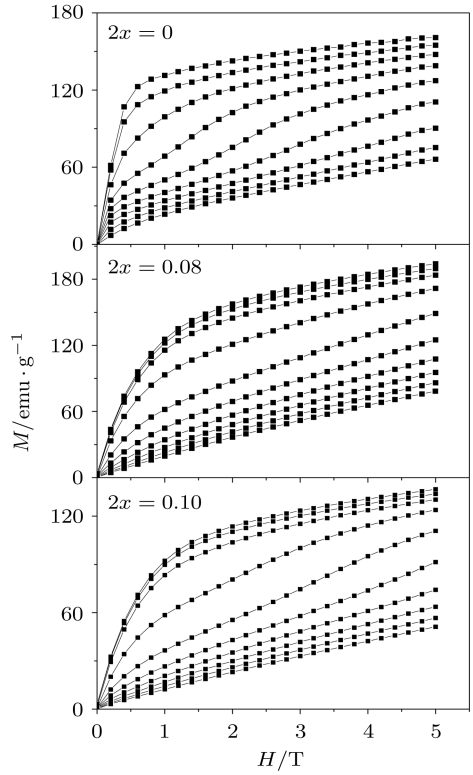


Fig. 4. Isothermal magnetization curves for $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08 and 0.10) compounds measured around T_C and in the magnetic field range of 0–5 T.

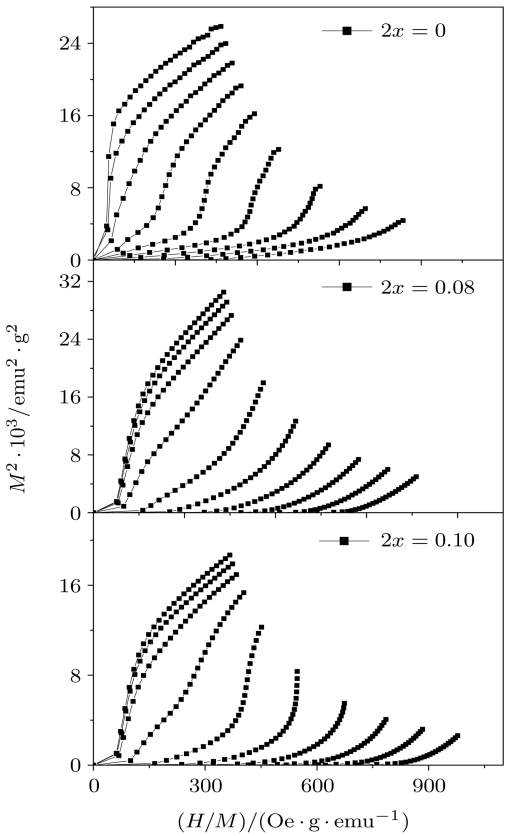


Fig. 5. The Arrott Plots of compounds $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10).

gradient) M^2–H/M curves near T_C is normally associated with first-order magnetic phase transitions.[19] A negative gradient is observed in parent and Mn doped compounds around T_C. Thus, we conclude that these non-alloyed and alloyed compounds exhibit first-order phase transition. Magnetic entropy change values of the alloyed compounds near their ordering temperature were calculated from magnetization isotherms using Eq. (2). These are presented in Fig. 6 and the maximum magnetic entropy change values are given in Table 2. The maximum isothermal magnetic entropy changes of $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) are 12.91, 19.64, 20.84 $J \cdot kg^{-1} \cdot K^{-1}$ respectively for a maximum magnetic field change from 0 to 5 T.

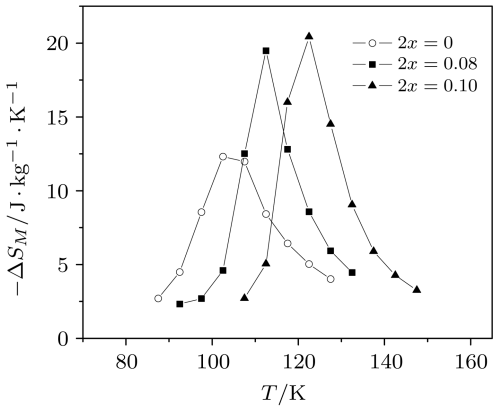


Fig. 6. Magnetic entropy change of $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) compounds as a function of temperature under a magnetic field of 5 T.

It is observed that all the compounds exhibit large MCE's. Practically, magnetic refrigerants are desired to have not only a large $\Delta S_M\ (T, H)$ but also a large refrigerant capacity value q defined by

$$q = \int_{T_1}^{T_2} \Delta S_M(T)\mathrm{d}T, \tag{3}$$

where q is a measure of heat transferred between thermal baths T_1 and T_2 in one ideal refrigeration cycle.[20]

The other parameter for characterization magnetocaloric properties is the relative cooling power (RCP) which is determined by the product of the peak value of the magnetic entropy change $(\Delta S_M)^{\max}$ and the full width at half maximum (FWHM) of ΔS_M[21] and is written as:

$$\mathrm{RCP} = -(\Delta S_M)^{\max}\delta T_{\mathrm{FWHM}}, \tag{4}$$

The calculated values of q and RCP are given in Table 2. Since RCP represents a good factor for comparing magnetocaloric materials, the Mn-substituted compound with $2x = 0.10$ looks very promising due to its high q and RCP values. ($q = 410.43\ \mathrm{J \cdot kg^{-1}}$ and $\mathrm{RCP} = 330.43\ \mathrm{J \cdot kg^{-1}}$)

Table 2. The spin reorientation temperatures (T_{sr}/K), the Curie temperatures (T_C/K), maximum isothermal magnetic entropy changes ($(\Delta S_M)^{\max}$/J·kg^{-1}·K^{-1}), refrigerant capacity (q/J·kg^{-1}) and relative cooling power (RCP/J·kg^{-1}) for the $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) compounds.

$2x$	T_C/K	T_{sr}/K	$(\Delta S_M)^{\max}$	q	RCP
0	111	70	12.91	358.82	320.88
0.08	113	88	19.64	373.22	280.67
0.1	123	102	20.84	410.43	330.43

3.3. Application of Landau theory

In the Landau theory of phase transitions framework, an expansion of the Gibbs free energy ($G(T, M)$) up to sixth power of the magnetization

$$G(T, M) = G_0 + \frac{1}{2}\alpha M^2 + \frac{1}{4}\beta M^4 + \frac{1}{6}\delta M^6 - MH \tag{5}$$

is used. The $\alpha(T)$, $\beta(T)$, $\delta(T)$ coefficients are temperature dependent. $\alpha(T)$ and $\beta(T)$ coefficients are used to determine the critical temperature and nature of the transition, respectively. If $\beta(T) < 0$, the transition is a first order transition and if $\beta(T) > 0$, it is a second order transition. This method is an appropriate model for explaining the magnetic phase transitions.[22] From energy minimization, the magnetic equation of state

$$\frac{H}{M} = \alpha + \beta M^2 + \delta M^4 \tag{6}$$

is derived which leads directly to the Arrott plots. For both samples, the expansion coefficients were determined by fitting the Arrott plots to the equation of state (Eq. (6)).[23] The values of $\alpha(T)$ and $\beta(T)$ are given in Figs. 7 and 8, respectively. From Fig. 7, the minimum values of $\alpha(T)$ occur around the T_C. From Fig. 8, the $\beta(T)$ values reveal the type of magnetic phase transition close to transition temperature. For $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) compounds the negative $\beta(T)$ values around T_C imply the first order magnetic phase transitions.

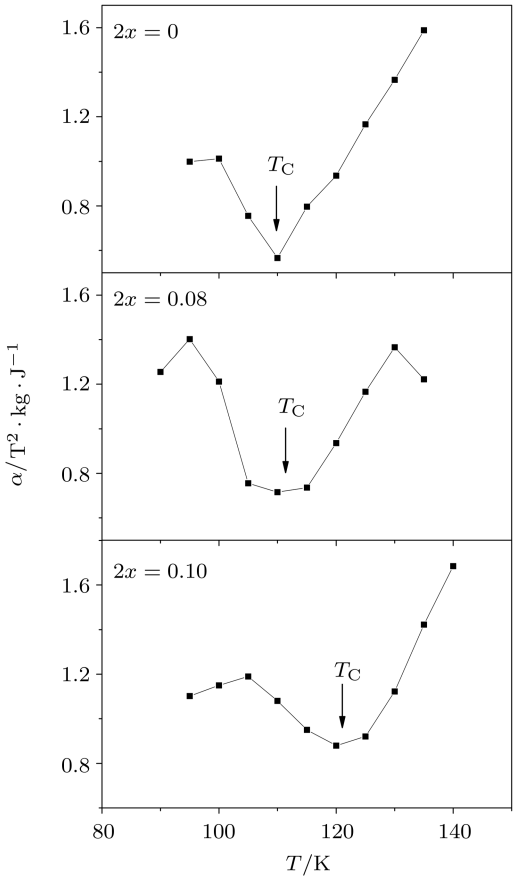


Fig. 7. The relation of $\alpha(T)$ with temperature for $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) compounds.

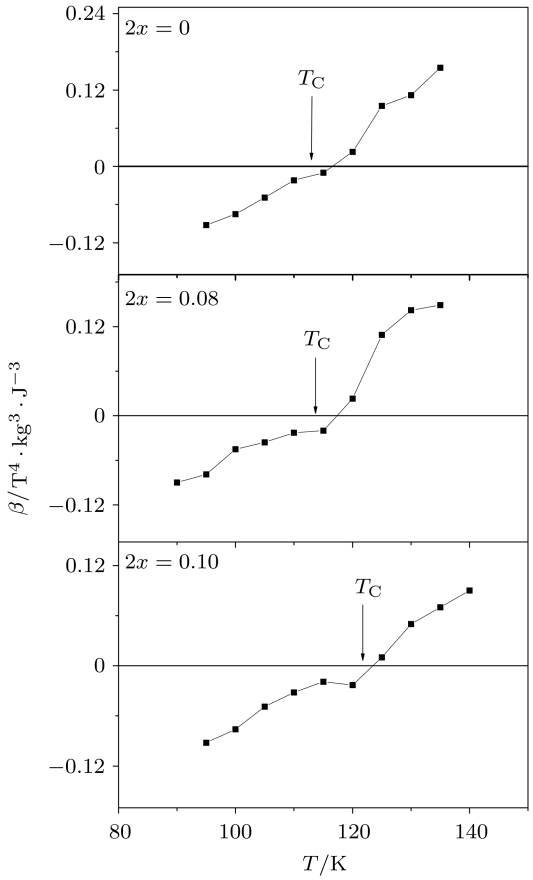


Fig. 8. The relation of $\beta(T)$ with temperature for $Tb_5Ge_{2-x}Si_{2-x}Mn_{2x}$ ($2x = 0$, 0.08, 0.10) compounds.

4. Conclusion

In this work, we have studied the structural, magnetic and magnetocaloric properties of Mn doped $Tb_5Si_2Ge_2$ compounds. Without altering the crystal structure we have doped Mn atoms with d energy levels in place of Si and Ge atoms that have s and p energy levels. However increasing Mn content has caused a decrease in the unit cell volume, and the increases of magnetization and isothermal magnetic entropy change values with respect to parent compound because the Mn atoms have magnetic moments whereas Si and Ge atoms do not. In our previous work where we had doped $Tb_5Si_2Ge_2$ with Fe, Pb and Sn, the unit cell volumes were observed to increase thus the magnetic interaction between magnetic ions decreased with regard to parent compound. As a result, isothermal magnetic entropy change around the transition temperatures decreased. The results of doping $Tb_5Si_2Ge_2$ with Mn, Fe, Pb and Sn are consistent with each other. The differences in magnetic behaviour can be explained by the Tb–(Si/Ge)(Si/Ge)–Tb interactions via changing of bond lengths which affect the RKKY indirect exchange interaction which is used to explain the 4f electron atoms.[24] We have verified the significance of Tb–(Si/Ge)(Si/Ge)–Tb interactions by explaining the magnetic characteristics of these systems.

References

[1] Warburg E 1881 *Ann. Phys.* **13** 141

[2] Pecharsky A O, Gschneidner Jr K A and Pecharsky V K 2003 *J. Appl. Phys.* **93** 4722

[3] Cam Thanh D T, Brück E, Tegus O, Llaasse J C P and Bushow K H J 2007 *J. Magn. Magn. Mater.* **310** e1012

[4] Mandal K, Pal D, Gutfleisch O, Kerschl P and Mler K H 2007 *J. Appl. Phys.* **102** 053906

[5] Pecharsky V K and Gschneidner Jr K A 2001 *Adv. Mater.*

(Weinheim) **13** 683
[6] Gschneidner Jr K A, Percharsky V K and Tsokol A O 2005 *Rep. Prog. Phys.* **68** 1479
[7] Morellon L, Magen C, Algarabel P A, Ibarra M R and Ritter C 2001 *Appl. Phys. Lett.* **79** 1318
[8] Ritter C, Morellon L, Algarabel P A, Magen C and Ibarra M R 2002 *Phys. Rev.* B **65** 094405
[9] Tegus O, Dagula O, Brck E, Zhang L, de Boer F R and Buschow K H J 2002 *J. Appl. Phys.* **91** 8534
[10] Huang H, Pecharsky A O, Pecharsky V K and Gschneidner Jr K A 2002 *Adv. Cryog. Eng.* **614** 11
[11] Thuy N P, Nong N V, Hien N T, Tai L T, Vinh T Q, Thang P D and Brck E 2002 *J. Magn. Magn. Mater.* **242** 841
[12] Yüzüak E, Emre B, Yücel A and Elerman Y 2009 *J. Alloys and Compounds* **476** 929
[13] Yüzüak E, Emre B, Dincer I, Ener S, Yücel A and Elerman Y 2009 *J. Optoelectron. Adv. Mater.* SYMPOSIA
[14] Buschow K H J (ed) 1991 *Handbook of Magnetic Materials* Vol 6 (Amsterdam, North Holland) p271
[15] Pecharsky V K and Gschneidner Jr K A 1999 *J. Appl. Phys.* **86** 565
[16] Zhang T, Chen Y, Teng B, Tang Y, Fu H and Tu M 2007 *Materials Letters* **61** 440
[17] Paudyal D, Percharsky V K, Gschneidner Jr K A and Harmon B N 2006 *Phys. Rev.* B **73** 1444061
[18] Krenke T, Acet M, Wassermann E F, Moya X, Manosa L and Planes A 2006 *Phys. Rev.* B **73** 174413
[19] Arrot A 1957 *Phys. Rev.* **108** 1394
[20] Pecharsky V K and Gschneidner Jr K A 2001 *J. Appl. Phys.* **90** 4614
[21] Gschneidner K A and Pecharsky V K 2000 *Annu. Rev. Mater. Sci.* **30** 387
[22] Inoue J and Shimizu M 1982 *J. Phys.* F **12** 1811
[23] Liu X B, Ryan D H and Altounian Z 2004 *J. Magn. Magn. Mater.* **270** 305
[24] Haskel D, Lee Y B, Harmon B N, Islam Z, Lang J C, Srajer G, Mudryk Ya, Gschneidner Jr K A and Pecharsky V K 2007 *Phys. Rev. Lett.* **98** 247205