Magnetocaloric effects in $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds*

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(Received 4 May 2011; revised manuscript received 29 September 2011)

The structural and magnetocaloric properties of $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds are investigated. The Si-substituted compounds, $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ with $x = 0.52$, 0.54, 0.55, 0.56, and 0.57, are prepared by high-energy ball milling and the solid-state reaction. The X-ray diffraction shows that the compounds crystallize into the Fe_2P-type hexagonal structure with space group $P\bar{6}2m$. The magnetic measurements show that the Curie temperature of the compound increases from 253 K for $x = 0.52$ to 296 K for $x = 0.56$. The isothermal magnetic-entropy change of the $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compound decreases with the Si content increasing. The maximal value of the magnetic-entropy change is about 7.0 J/kg·K in the $Mn_{1.35}Fe_{0.65}P_{0.48}Si_{0.52}$ compound with a field change of 1.5 T. The compound quenched in water possesses a larger magnetic entropy change and a smaller thermal hysteresis than the non-quenched samples. The thermal hysteresis of the compound is less than 3.5 K. The maximum adiabatic temperature change is about 1.4 K in the $Mn_{1.35}Fe_{0.65}P_{0.45}Si_{0.55}$ compound with a field change of 1.48 T.

Keywords: magnetocaloric effect, magnetic-entropy change

PACS: 75.50.–y, 43.40.–r, 75.30.Sg **DOI:** 10.1088/1674-1056/21/3/037504

1. Introduction

Room-temperature magnetic refrigeration, which is based on the magnetocaloric effect (MCE), has attracted much attention because of its potential energy savings and environmental friendliness.[1−3] The current investigation of the magnetocaloric effect focuses on the paramagnetic (PM)-ferromagnetic (FM) first-order phase transition materials, such as $Gd_5(Ge_{1-x}Si_x)_4$,[4] $MnAs_{1-x}Sb_x$,[5] $La(Fe_{1-x}Si_x)_{13}$ and its hydrides,[6−9] $MnCoGeB_x$,[10] and $PrFe_{12}B_6$.[11] These materials exhibit large values of magnetic entropy change ($-\Delta S_m$) in the vicinity of the magnetic-phase transition from the paramagnetic state to the ferromagnetic state. In particular, Tegus *et al.*[12] found that $MnFeP_{1-x}As_x$ compounds with a hexagonal Fe_2P-type structure each exhibit a large MCE, which originates from the first-order PM-FM phase transition.[12] This result shows that a giant MCE in a material not only results from the large magnetic moment in the material, but also depends on the type of the phase transition. So the $MnFeP_{1-x}As_x$ compound becomes one of the potential candidate materials for room temperature magnetic refrigeration due to their low-cost raw materials, simple preparation, and proper working temperature. In order to avoid using As, a great deal of work has been done to replace As by Ge or Si.[13−21] Dagula *et al.*[16] found a giant MCE in $Mn_{1.1}Fe_{0.9}P_{1-x}Ge_x$ compounds, and Trung *et al.*[14] reported a giant MCE in the $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ compound. In the $Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$ compound, the thermal hysteresis (ΔT_{hys}) can be reduced to 1 K, the maximal value of magnetic-entropy change ($-\Delta S_{max}$) is about 20 J/kg·K with a field change of 2 T. Ge is so expensive that the material containing Ge is not suitable for most applications. Recently, the Si-substituted MnFe(P, Si) compounds have drawn much attention due to their excellent MCE properties and low material cost. The $MnFeP_{1-x}Si_x$ compound exhibits a large MCE (up to 30 J/kg·K for a field change from 0 T to 2 T), but ΔT_{hys} of the $MnFeP_{1-x}Si_x$ compound is quite large.[21] Geng *et al.*[19] reported a $-\Delta S_{max}$ of 13.9 J/kg·K (in a field change of 1.5 T) in the $Mn_{2-x}Fe_xP_{0.51}Si_{0.49}$ compound, and found that the ratio of Fe/Mn plays an important role in tuning ΔT_{hys}. In this paper, we report on a significant reduction of ΔT_{hys} and the direct measurement results of the MCE in the $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds

*Project supported by the National Natural Science Foundation of China (Grant No. 50961010) and the Natural Science Foundation of Inner Mongolia, China (Grant No. 20080404Zd01).

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with $x = 0.52$, 0.54, 0.55, 0.56, and 0.57.

2. Experiments

$Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds with $x = 0.52$, 0.54, 0.55, 0.56, and 0.57 (nominal composition) were synthesized with high-energy ball milling by using the solid state reaction method. The starting materials, Mn (purity 99.9%), Si (purity 99.999%), red P (purity 99.999%), and Fe powder (purity 99.8%), were milled under the N_2 atmosphere in a high-energy ball mill for 5 h. They were milled into powder. Then the powder was pressed into pellets (under a pressure of 3.9×10^8 Pa) and sealed in quartz ampoules in an Ar atmosphere of 2×10^4 Pa. Then, the ampoules were sintered at 1100 °C for 2 h and homogenized at 850 °C for 20 h. Finally, they were slowly cooled down to room temperature. The samples with $x = 0.56$ and 0.57 were also quenched in water after being sintered at 1100 °C for 10 h. The powder X-ray diffraction (XRD) of the samples was performed at room temperature by using a Philips PW1830 diffractometer with the Cu $K\alpha$ radiation. The magnetization measurements were carried out by using a Lakeshore 7407 type vibrating sample magnetometer (VSM). The direct measurement of the adiabatic temperature change was performed by using home-built equipment at the Baotou Institute for Rare Earths.

3. Results and discussion

The XRD patterns of the $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds with $x = 0.52$, 0.54, 0.55, 0.56, and 0.57 are shown in Fig. 1. Analysis of the XRD patterns shows that the compounds all crystallize into the Fe_2P-type hexagonal structure (space group $P\bar{6}2m$). A small amount of secondary phase $(Mn,Fe)_5Si_3$ (indicated by the arrows) is detected both in the $Mn_{1.35}Fe_{0.65}P_{0.46}Si_{0.54}$ compound cooled in the furnace and in the $Mn_{1.35}Fe_{0.65}P_{0.44}Si_{0.56}$ compound quenched in water, and no detectable trace of the second phase is found in the other compounds. The lattice parameters a and c and the c/a ratio are listed in Table 1.

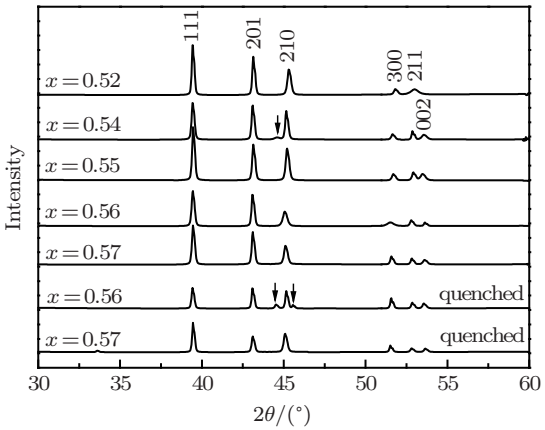


Fig. 1. X-ray diffraction patterns of $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds, the compounds quenched in water are marked as quenched.

Table 1. Lattice parameters a and c, c/a ratio, Curie temperature, thermal hysteresis, maximum isothermal magnetic entropy change with $\Delta B = 1.5$ T, and maximum adiabatic temperature change with $\Delta B = 1.48$ T of $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds obtained in different heat treatment processes (quenched samples are denoted by q).

x	a/nm	c/nm	c/a	T_C/K	ΔT_{hys}/K	$-\Delta S_{max}$/J·kg^{-1}·K^{-1}	ΔT_{ad}^{max}/K
0.52	0.6109	0.3435	0.5623	253	2.0	7.0	–
0.54	0.6129	0.3421	0.5582	275	3.5	4.0	1.2
0.55	0.6122	0.3425	0.5594	280	3.5	4.2	1.4
0.56	0.6145	0.3415	0.5557	296	3.5	3.3	1.2
0.57	0.6136	0.3417	0.5561	289	3.5	3.5	–
0.56(q)	0.6133	0.3412	0.5563	278	2.0	4.3	–
0.57(q)	0.6140	0.3414	0.5560	293	2.0	4.2	–

Figure 2 shows the temperature dependences of magnetization (M–T) of the $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds with $x = 0.52$, 0.54, 0.55, 0.56, and 0.57 (in a field of 0.05 T). The ΔT_{hys} between the heating and the cooling processes for all compounds ranges from 2 K to 3.5 K. These values are much smaller than the previously reported values in the MnFe(P, Si) compounds. The compounds quenched in water possess smaller ΔT_{hys} compared with the samples without the quenching. The results are displayed in Table 1. The T_C values of the compounds furnace-cooled are 253 K, 275 K, 280 K, 296 K, and 289 K for the $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds with $x = 0.52$, 0.54, 0.55, 0.56, and 0.57, respectively. The smaller c/a ratio corresponds to the higher T_C in the single-phase compound (see Fig. 3). The change

of T_C follows inversely the change of the c/a ratio, indicating that the exchange interaction between the Fe–Mn plays an important role in determining T_C. This result is in good agreement with the previous results of $MnFeP_{1-x}Si_x$, $MnFeP_{0.5}As_{0.5-x}Ge_x$, and $MnFe(P_{0.89-x}Si_x)Ge_{0.11}$ compounds.[15,21,22] The T_C values of the compounds quenched in water are 278 K and 293 K for $x = 0.56$ and 0.57, respectively. The changing rate of the M–T curve from the FM state to the PM state can determine the value of $-\Delta S_m$, so it also indicates from Fig. 2 that $-\Delta S_{max}$ in the $Mn_{1.35}Fe_{0.65}P_{0.48}Si_{0.52}$ compound would be larger than that in the other $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds.

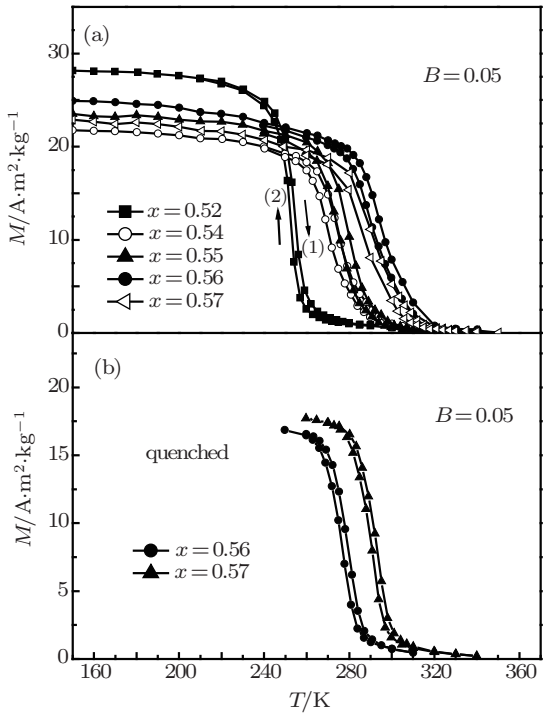


Fig. 2. Temperature dependences of magnetization of (a) as-prepared and (b) water quenched $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds. Measurement is performed by heating (1) and subsequent cooling (2) the samples in a field of 0.05 T.

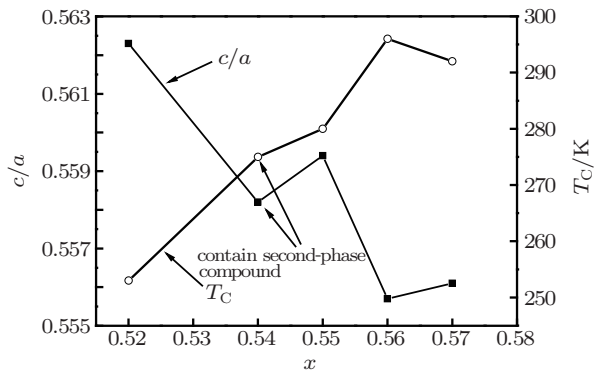


Fig. 3. Ratio c/a and Curie temperature versus x.

The field-dependent magnetization curves of the $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds with $x = 0.52$, 0.54, 0.55, and 0.56 measured in an increasing field in the vicinity of T_C are shown in Fig. 4. The results show that the magnetization of the compound decreases with the increase of the Si content in the furnace-cooled compound, this is because the Si substituting P would make the distance between the Mn and the Fe layers larger, thereby reducing the FM exchange interaction between Mn and Fe. We do not observe any field-induced transition for a magnetic field up to 1.5 T in all compounds. The -ΔS_m can be derived by using the Maxwell relation, and it is expressed as

$$\Delta S_m(T, \Delta B) = S_m(T, B) - S_m(T, 0) = \int_0^B \left(\frac{\partial M}{\partial T}\right)_{B'} dB'. \quad (1)$$

For the magnetization measurements performed at discrete temperatures, ΔS_m can be calculated numerically by

$$\Delta S_m(T, \Delta B) = \sum_i \frac{M_i(T + \Delta T/2, B_i) - M_i(T - \Delta T/2, B_i)}{\Delta T} \Delta B_i, \quad (2)$$

where $M_i(T + \Delta T/2, B_i)$ and $M_i(T - \Delta T/2, B_i)$ represent the values of magnetization in magnetic field B_i at temperatures $T + \Delta T/2$ and $T\Delta T/2$, respectively, and ΔB is the final field change.

Figure 5 displays the temperature dependences of $-\Delta S_m$ of the $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds with a field change of 1.5 T. The values of $-\Delta S_m$ are 7.0 J/kg·K, 4.0 J/kg·K, 4.2 J/kg·K, 3.3 J/kg·K, and 3.5 J/kg·K for $x = 0.52$, 0.54, 0.55, 0.56, and 0.57, respectively. Here, we focus our attention on $-\Delta S_{max}$ that sharply decreases from 7.0 J/kg·K to 4.0 J/kg·K with the content of Si increasing from 0.52 to 0.54. However, the values of $-\Delta S_{max}$ for the compounds are larger than that of Gd, the value of the half peak is increscent with the content of Si increasing. The $-\Delta S_{max}$ is effectively enhanced in the $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compound after quenching in water, the maximal values are 4.3 J/kg·K and 4.2 J/kg·K for $x = 0.56$ and 0.57, respectively. Figure 6 displays the temperature dependences of the adiabatic temperature change (ΔT_{ad}) of the $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds with $x = 0.54$, 0.55, and 0.56 in a field changing from 0 T to 1.48 T. The maximal adiabatic temperature changes (ΔT_{ad}^{max}) are about 1.2 K, 1.4 K, and 1.2 K for $x = 0.54$, 0.55, and 0.56, respectively. These values are larger than that of the $Ni_{50.2}Mn_{39.8}In_{10}$ compound (ΔT_{ad}^{max} is about 1.15 K for a field change of 1.48 T).[23]

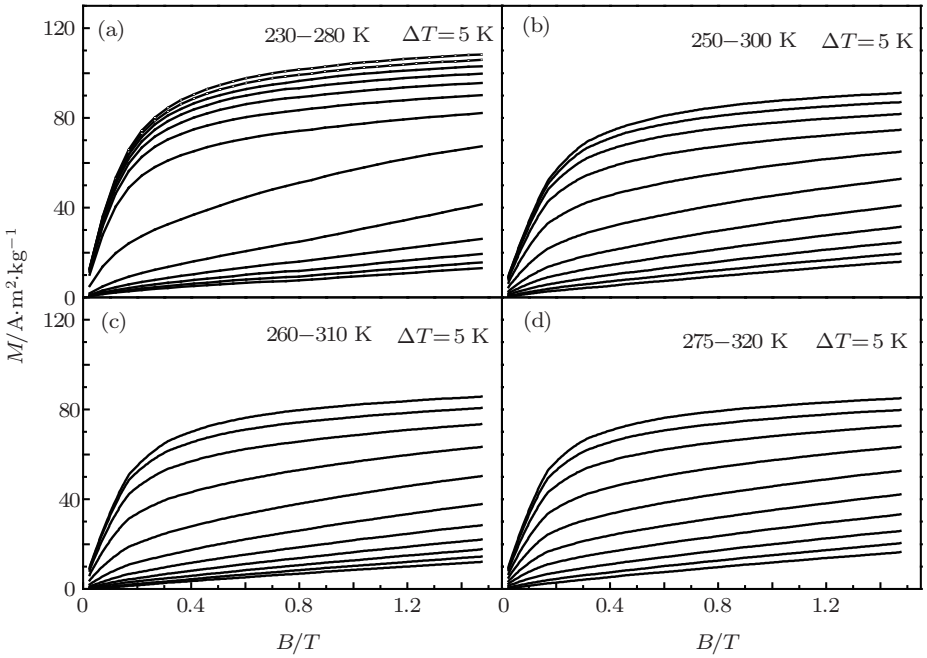


Fig. 4. Isothermal magnetizations of furnace-cooled $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds with x equaling to (a) 0.52, (b) 0.54, (c) 0.55, and (d) 0.56.

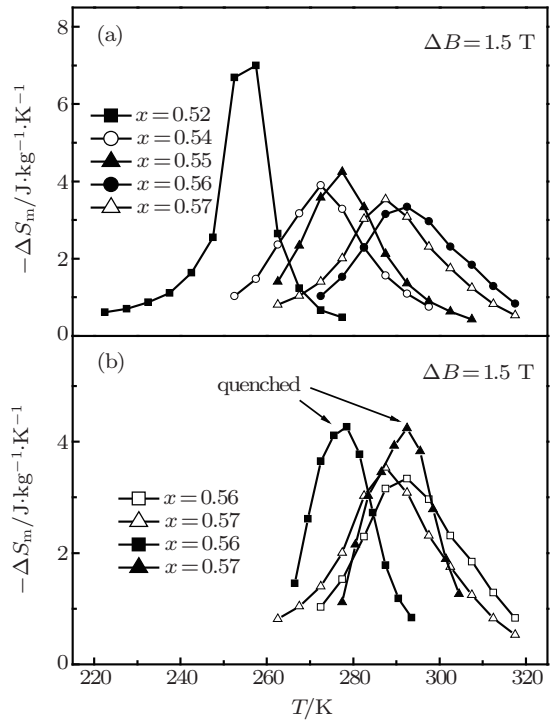


Fig. 5. Isothermal magnetic-entropy changes of (a) furnace cooled $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds (x = 0.52, 0.54, 0.55, 0.56, and 0.57) and (b) $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds (x = 0.56 and 0.57) obtained in different heat treatment processes. External field change is 1.5 T.

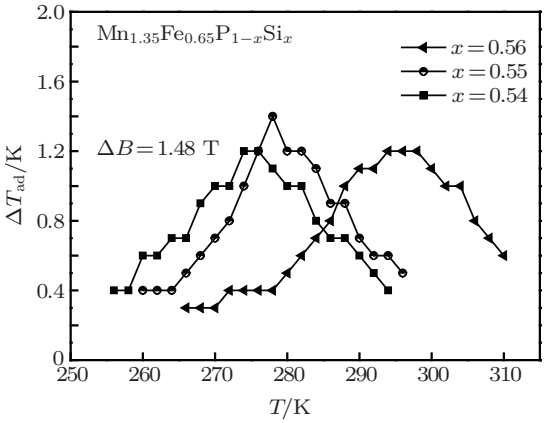


Fig. 6. Temperature dependences of adiabatic temperature change of furnace cooled $Mn_{1.3}Fe_{0.7}P_{1-x}Si_x$ compounds (x = 0.54, 0.55, and 0.56) with a field change of 1.48 T.

4. Conclusion

$Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compounds with x = 0.52, 0.54, 0.55, 0.56, and 0.57 are prepared by ball milling in the N_2 atmosphere and the solid-state reaction. The interplay between the structure and the magnetism plays an important role in changing the magnetic entropy of the $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$ compound. A proper heat treatment method is effective for reducing the thermal hysteresis and enhancing the magnetic-entropy change in the $Mn_{1.35}Fe_{0.65}P_{1-x}Si_x$

compound. The adiabatic temperature change of the compound is about 1 K/T near room temperature. These excellent features of the MCE in these compounds, in addition to the low material cost, make them promising candidate materials for room-temperature magnetic refrigeration applications.

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