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Magnetocaloric effects and reduced thermal hysteresis in Si-doped MnAs compounds

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ABSTRACT

The magnetocaloric effects in $MnAs_{1-x}Si_x$ ($x = 0.03$, 0.06 and 0.09) compounds have been investigated. The Curie temperature can be tunable in a wide range by changing the Si content. With increasing Si doping, the thermal hysteresis is decreased to nearly zero ($x > 0.06$) and the metamagnetic transition becomes ambiguous, being a second-order-like one. The maximum of the magnetic entropy change is maintained above $10\,J\,kg^{-1}\,K^{-1}$ and $5\,J\,kg^{-1}\,K^{-1}$ in $MnAs_{1-x}Si_x$ for the field change of 5 T and 2 T, respectively. These results indicate that the Si-doped MnAs compounds with reduced thermal hysteresis are potential candidates of the room-temperature magnetic refrigeration.

1. Introduction

The magnetocaloric effect (MCE) means the isothermal entropy change or the adiabatic temperature change by a magnetic field. Magnetic refrigeration is considered as a kind of potential technology to replace common gas-compression/expansion technology because of high-efficiency and environmental concerns. In order to realize this purpose, it is important to explore compounds with large entropy changes near room temperature. Some systems undergoing a first-order magnetic transition were found to exhibit a large MCE [1–3], which was contributed partly from the difference of magnetic orderings in two adjacent magnetic phases.

MnAs is a ferromagnet with its Curie temperature $T_c = 318$ K. The ferromagnetic–paramagnetic transition is of first-order, which is accompanied by a structural transition from hexagonal type to orthorhombic type [4]. A large entropy change of $40\,J\,kg^{-1}\,K^{-1}$ was reported in $MnAs_{1-x}Sb_x$ for a field change of 5 T, and the corresponding adiabatic temperature change ΔT_{ad} was 13 K [5]. Later, it was found that both the magnitude of entropy change and the Curie temperature T_c were very sensitive to the external pressure [6]. A large entropy change was discovered by substitution of Cu [7] and Fe [8] for Mn in the MnAs alloy. In our recent work [9], it was revealed that interstitial effect can also act as a kind of lattice pressure, similar to the effect of substitution. However, a remarkable disadvantage in the MnAs-based systems is the large thermal hysteresis, which is harmful to applications. Up to date, most investigations have been focused on the substitution of transition metals for Mn, except for $MnAs_{1-x}Sb_x$ [5]. It was reported that other substitutions, such as S, Se, Te, Bi and P, present low solubility or no MCE by sintering process [7]. Compared with solid-state reaction, mechanical alloying is a useful method to prepare metastable phases. It is possible to carry out research on unstable or metastable phases with concentration over the solubility limit, which cannot be synthesized by the solid-state reaction. In the present paper, the main-group element Si is used to replace portion of As in MnAs. The Si substitution leads to a second-order-like phase transition so that the large thermal hysteresis in MnAs is reduced to nearly zero in $MnAs_{1-x}Si_x$ alloys. The results indicate that Si-doped MnAs compounds with reduced thermal hysteresis are potential candidates of the room-temperature magnetic refrigeration.

2. Experimental

Raw materials Mn, As, Si with purity higher than 99.9% were mixed according to the composition of $MnAs_{1-x}Si_x$ ($x = 0.03$, 0.06 and 0.09), which

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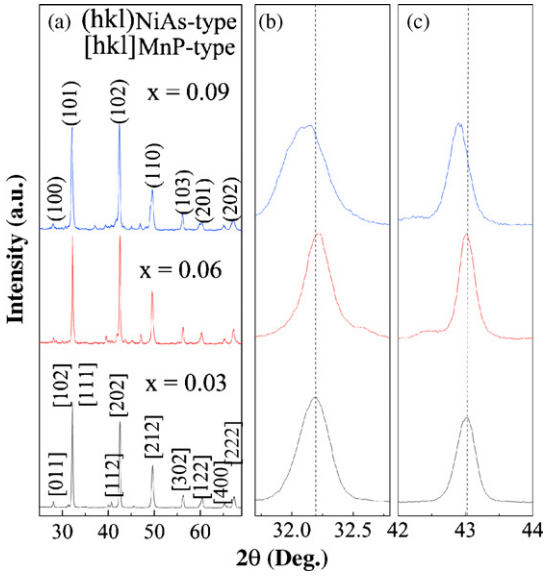

Fig. 1. (a) XRD patterns and the step-scanned XRD patterns from (b) 31.5° to 33.5° and (c) 41.5–43.5° at room temperature of $MnAs_{1-x}Si_x$ (x = 0.03, 0.06 and 0.09) compounds.

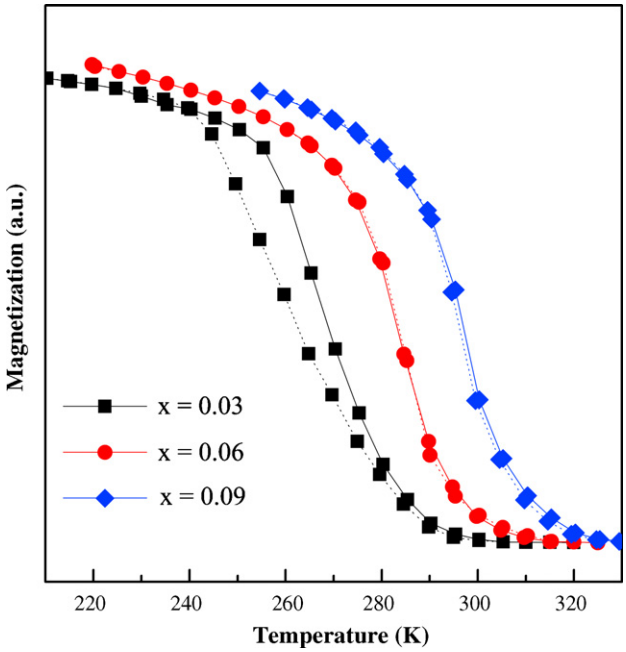

Fig. 2. Temperature dependences of magnetization for $MnAs_{1-x}Si_x$ (x = 0.03, 0.06 and 0.09) at 0.01 T. The solid and dash lines represent the heating and cooling processes.

were mechanical alloyed in order to avoid the volatilization of As and time-exhausting solid-state reaction. The mixtures of 10 g were sealed in hardened stainless steel vials with stainless steel balls of 12 mm diameter in a glove box filled with high purity argon. The mechanically alloyed powders were annealed at 773 K for 2 h and then at 923 K for 2 h in vacuum better than 10^{-3} Pa. X-ray diffraction (XRD) analysis was conducted using Cu Kα radiation with a Rigaku D/Max-γA diffractometer equipped with a graphite crystal monochromator. The magnetic properties were measured using a superconducting quantum interference device (SQUID) with fields up to 5 T. The magnetic entropy change was calculated from M–B plots close to their respective Curie temperature T_c.

3. Results and discussions

Fig. 1 shows the XRD patterns at room temperature of $MnAs_{1-x}Si_x$ compounds (x = 0.03, 0.06 and 0.09). It can be seen from Fig. 1(a) that the structure at room temperature of the main phase changes from the MnP-type structure in $MnAs_{0.97}Si_{0.03}$ and $MnAs_{0.94}Si_{0.06}$ to NiAs-type structure in $MnAs_{0.91}Si_{0.09}$. Because the compound with the NiAs-type structure is ferromagnetic and that with the MnP-type structure is paramagnetic, such structural change means that the Curie temperature T_c of $MnAs_{1-x}Si_x$ (x = 0.03, 0.06 and 0.09) is increased from below to above room temperature by the Si substitution. The MnAs phase can be formed with Si content as high as 9%, much larger than that of other reported elements [5–8]. Fig. 1(b) and (c) shows the refined XRD patterns from 31.5° to 33.5° and 41.5–43.5°. It can be seen that the peaks moves to smaller angles with increased Si content. If such shift is caused by the different atomic size of Si and As, the peaks should move to higher angles. Therefore, such shifts to lower angle in the refined XRD patterns further confirm the structure transformation from MnP-type structure to NiAs-type structure.

In order to make clear the effect of Si substitution on the transition between magnetic phases, the M–T curves were recorded at 0.01 T for $MnAs_{1-x}Si_x$ (x = 0.03, 0.06 and 0.09) compounds, as shown in Fig. 2. Combined with our recent results on mechanical alloyed Al-substituted $Mn_{1-x}Al_xAs$ powders where the Curie temperature of mechanical alloyed MnAs mother alloy is about 220 K measured in the heating process [10], the Curie temperature increases monotonically with increasing the Si content in $MnAs_{1-x}Si_x$, which is in agreement with the XRD results above. It is worth noticing that the thermal hysteresis diminishes gradually from about 10 K in $MnAs_{0.97}Si_{0.03}$ to nearly zero in $MnAs_{0.91}Si_{0.09}$. Compared with the thermal hysteresis in MnAs and other substituted alloys [5–10], it is concluded that the Si substitution is beneficial to decrease the thermal hysteresis, which is important to practical applications.

In order to investigate the influence of Si substitution on the MCE, M–B curves of $MnAs_{1-x}Si_x$ (x = 0.03, 0.06 and 0.09) compounds are recorded near their respective Curie temperature T_c. It can be seen from Fig. 3 that the magnetization increases rapidly and shows a tendency to saturate at a low field, indicating a stable FM state with NiAs-type structure. With increasing temperature, an inflexion can be observed on the magnetization curves, indicating a metamagnetic phase transition accompanied by a structural transition from paramagnetic MnP-type orthorhombic structure to ferromagnetic NiAs-type hexagonal structure. However, such increment on magnetization induced by the external field is not as obvious as that in other systems with large thermal hysteresis [5–10]. It is more analogous to a second-order phase transition, which is considered to relate closely with reduced thermal hysteresis. Moreover, with increased silicon content from 0.03 to 0.06 and 0.09, the saturation content is greatly decreased near respective Curie temperatures.

The isothermal ΔS is given by the Maxwell relationship: $\Delta S(T) = \int_0^B (\partial M/\partial T)_B \, dB$. The temperature dependences of $\Delta S(T)$ for $MnAs_{1-x}Si_x$ (x = 0.03, 0.06 and 0.09) compounds for a field change of 5 T and 2 T are shown in Fig. 4. A broad peak can be seen near the respective Curie temperature T_c on the $\Delta S(T)$–T curves, dislike the sharp peak ever reported in Fe or Cu substituted MnAs systems where the phase transition is typically of first-order accompanied with a large hysteresis [7,8]. It can be seen from Fig. 4 that in $MnAs_{0.97}Si_{0.03}$, the maximum of