Magnetic and magnetocaloric properties of $Mn_{0.98}Fe_{0.02}P_{1-x}As_x$ compounds

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ABSTRACT

MnP has been subject of considerable attention due to its wealth of magnetic phases and complex magnetic transitions in the presence of a magnetic field and at high pressure. In the present polycrystalline $Mn_{0.98}Fe_{0.02}P_{1-x}As_x$ (with x = 0, 0.05 and 0.1) compounds, prepared by mechanical milling, a slight Fe doping lowers the Curie temperature T_C from 291 K for MnP to 270 K and the T_C is increased remarkably to 295 K through further replacing P by a small amount of As. In accordance with the ferromagnetic-paramagnetic transition, magnetocaloric effect (MCE) without thermal hysteresis is observed over a wide temperature range around room temperature. The maximum value of the magnetic-entropy change is 2.4 J/kg K for $Mn_{0.98}Fe_{0.02}P_{0.9}As_{0.1}$ at 300 K for a field change from 0 to 5 T. In addition, around the transition temperature of the ferromagnetic phase to screw phase, an external field can induce a first-order magnetic transition from the screw state to fan state and, for $Mn_{0.98}Fe_{0.02}P$, an inverse MCE with a maximal magnetic-entropy change $\Delta S_m = 0.67$ J/kg K for a field change of 3 T at 92 K has been found.

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1. Introduction

At ambient conditions, MnP has the orthorhombic B31-type of crystal structure and exhibits two successive first-order magnetic transitions upon cooling: a transition from the paramagnetic (PM) to the ferromagnetic (FM) state at $T_C = 291$ K, and then a second transition to a screw (SCR) state at $T_s = 47$ K [1,2]. In the SCR state, the Mn spins have rotated in the bc plane, with a propagation vector q along the a axis [3]. Hydrostatic-pressure studies on MnP have shown that both T_s and T_C decrease with increasing pressure [4]. Upon increase of the pressure to 8 GPa the long-range magnetic order vanishes and the compound becomes superconducting [5]. In the presence of external magnetic fields, around T_s MnP shows a variety of magnetic structures, including FM, SCR, and fan (FAN) structure [6]. In the FAN structure, the spin does not perform a full rotation in bc plane but, instead, it oscillates around the b axis like a fan [7]. Based on the wealth of magnetic phases, MnP-based compounds exhibit interesting physical properties [8,9]. Very recently, a positive magnetoresistance ratio as large as 126% was observed at

2 K at 5 T in $MnP_{0.8}B_{0.2}$ [10] and pressure-induced superconductivity with $T_{sc} = 1$ K has been found in MnP, the first Mn-based superconductor [5]. In particular, a room-temperature magnetocaloric effect (MCE) originating from strong magnetocrystalline anisotropy with a maximal magnetic-entropy change $\Delta S_m = 6$ J/kg K for a field change of 5 T, has been found for a MnP single crystal [7,11].

Thus far, substitution of transition-metal elements, such as Fe and Cr [2,12], for Mn and B for P [10] lowers the T_C of MnP. In this paper, polycrystalline $Mn_{0.98}Fe_{0.02}P_{1-x}As_x$ compounds have been prepared by simple mechanical-milling process. Slight doping of 10% As for P remarkably increases the T_C of 270 K for $Mn_{0.98}Fe_{0.02}P$ to 295 K and a room-temperature MCE without thermal hysteresis was found with $\Delta S_m = 2.4$ J/kg K at 300 K for a field change of 5 T in $Mn_{0.98}Fe_{0.02}P_{0.9}As_{0.1}$. As doping shifts the T_s of MnP to lower temperatures and simultaneously increases the thermal hysteresis of the SCR-FM transition. Few references have reported MCEs originating from a SCR-FM transition [13]. In the present $Mn_{0.98}Fe_{0.02}P_{1-x}As_x$ compounds, around T_s, an external field can induce a first-order magnetic transition from the SCR state to the FAN state and, at 92 K, an inverse MCE with $\Delta S_m = 0.67$ J/kg K for a field change of 3 T for $Mn_{0.98}Fe_{0.02}P$ has been found.

2. Experimental

Polycrystalline $Mn_{0.98}Fe_{0.02}P_{1-x}As_x$ compounds with x = 0, 0.05 and 0.1 have been prepared by mechanical milling to avoid evaporation of As or P followed by long reaction-sintering heat treatment [14]. Mixtures of 5 g of Mn, Fe, P and As powders with purity of 99.9% were sealed in hardened-steel vials with steel balls of 12 mm diameter in a glove box filled with high-purity argon. The ball to powder weight ratio is 20:1. Mechanical alloying of the mixtures was carried out for 5–50 h using a high-energy ball-mill machine with a rotational speed of 800 rpm. During the milling process, not any stop was made. The mechanically alloyed powders were first slowly heated to 200 °C and held at this temperature for 3 h in a vacuum furnace. After this, the powders were annealed at 700 °C for another 3 h in an evacuated silica tube and then gradually cooled to room temperature.

X-ray diffraction (XRD) measurements of the $Mn_{0.98}Fe_{0.02}P_{1-x}As_x$ compounds were performed on a Rigaku DMAX/2000 diffractometer and a rotating Cu target was used with a voltage of 50 kV and a current of 150 mA. The magnetic properties were measured at applied magnetic fields up to 6 T by means of a superconducting quantum interference device (SQUID) magnetometer. The morphology and size distribution of the samples were examined by means of a Hitachi-3400N scanning electron microscope (SEM).

3. Results and discussion

3.1. Phase formation and structure

Earlier, polycrystalline MnP-based compounds have been synthesized by a long reaction-sintering treatment at about 1100 °C for more than one week [12]. Single-phase MnAs-based compounds have been successfully prepared in our previous work by a simple and time-saving mechanical-milling process [13]. In order to obtain single-phase MnP phase by the mechanical-milling method, we have first optimized the milling time. Fig. 1(a) shows the XRD profiles of selected reflections of $Mn_{0.98}Fe_{0.02}P$ samples with milling times varying from 5 to 50 h. The samples consist of orthorhombic MnP phase and hexagonal Mn_2P phase. Clearly, in the sample milled for 5 h, Mn_2P phase is the dominant phase with a weight fraction of 63%. Upon further increase of milling time, the intensities of the MnP phase reflections increase, indicating precipitation of a large amount of MnP phase from the Mn_2P phase. As shown in Fig. 1(c), the proportion of MnP phase reaches an optimum of 93% for the sample at a milling time of 24 h. With further increase of milling time, the Mn_2P phase precipitates. It is understandable that, in any milling process, part of the energy delivered to the material is stored as thermal energy which leads to a local increase of temperature of the powders, which influences the formation of the MnP and Mn_2P phases. Similar phase formation and decomposition has been found in the milling process of MnBi [15]. In view of the evaporation of P, an excess (1%–3%) of P was added and then the samples were milled for the optimal 24 h to obtain single-phase MnP-phase compounds without secondary phases such as Mn_2P or $Mn_{5.64}P_3$ [16]. The XRD patterns of the samples and the weight fraction of Mn_2P are shown in Fig. 1(b) and (d).

Fig. 2(a) shows the XRD pattern of the as-prepared $Mn_{0.98}Fe_{0.02}P_{1-x}As_x$ compounds. It can be seen that upon substitution of As for P, the reflections of the orthorhombic B31-type structure shift to lower angles, indicating larger lattice parameters. The Rietveld profile refinement method [17] was used in order to determine the structural data as reported in Table 1. It is worth noting that the lattice parameters, a = 5.93 Å, b = 5.28 Å and c = 3.19 Å of $Mn_{0.98}Fe_{0.02}P_{0.9}As_{0.1}$ are larger than those of MnP with a = 5.92 Å, b = 5.26 Å and c = 3.17 Å [7]. Fig. 2(b) shows the

surface morphology of the sample prepared by mechanical milling. The SEM image shows that the $Mn_{0.98}Fe_{0.02}P_{0.9}As_{0.1}$ grains are nearly spherical and there exist some agglomerations with lighter contrast. This may originate from the presence of some small amount of secondary phases, possibly Mn_2P phase, which cannot be detected by XRD. Higher manganese silicide with composition of $MnSi_{1.74}$, which was prepared by mechanical milling for 54 h [18], show very similar morphology and agglomerations as the present $Mn_{0.98}Fe_{0.02}P_{0.9}As_{0.1}$ sample.

In case of manganite, magnetic and magnetocaloric properties are primarily related to the ratio of Mn^{3+}/Mn^{4+} [19]. Usually, the Mn^{4+} amount is tuned by aliovalent cation doping on the A site of the manganite perovskite structure. Another way to change the ratio is the variation of the oxygen content [20]. In order to check the effect of the substitution of As for P on the percentage of Mn cations, the valence of the Mn atoms has been studied by X-ray photoelectron spectroscopy (XPS). The binding energy peak for Mn^{4+} was not observed in the XPS spectrum (not shown here), and the percentage of Mn^{3+} does not change after substitution. In the MnP type T(P, As) alloys (T = Mn, Fe, Co, Cr), the valance state of As and P is −3 and the valance state of transition metals is +3 [12]. In addition, FeAs is a stable compound with the same MnP orthorhombic structure [21]. So it is well expected that the substitution does not influence the percentage of Fe cations.

3.2. Magnetic properties

To investigate the effect of As and Fe doping on T_s and T_C of MnP, the temperature dependence of the magnetization of $Mn_{0.98}Fe_{0.02}P_{1-x}As_x$ was measured from 10 to 350 K in a field of 0.02 T in a zero-field cooling process (ZFC) and in a field-cooling process (FC) (as shown in Fig. 3 (a) for $Mn_{0.98}Fe_{0.02}P$, (b) for $Mn_{0.98}Fe_{0.02}P_{0.95}As_{0.05}$ and (c) for $Mn_{0.98}Fe_{0.02}P_{0.9}As_{0.1}$). It can be clearly seen that the FC results display a comparatively large residual magnetization of more than 0.7 Am^2/kg at 10 K, showing SCR behavior at low temperatures. The M(T) curves of the three samples are very similar: in the ZFC process, upon warming, the magnetization increases and then reaches a maximum, showing the SCR-FM transition. With further increase of the temperature, the magnetization decreases and an FM–PM transition occurs at T_C. The phase-transition temperatures, T_s and T_C are defined as the temperatures at which the first derivative of the magnetization with respect to temperature (dM/dT) has its maximum and minimum value, respectively (as shown in the inset of Fig. 3). Substitution of 2% Fe lowers the T_C of MnP from 291 K to 270 K and, in contrast, the substitution of As for P remarkably shifts T_C to higher temperatures of 285 K for x = 0.05 and 295 K for x = 0.1. Meanwhile, upon the substitution of As for P, T_s decreases remarkably from 100 K for $Mn_{0.98}Fe_{0.02}P$ to 70 K for $Mn_{0.98}Fe_{0.02}P_{0.9}As_{0.1}$, as shown in Table 1. The values for T_s and T_C of $Mn_{0.98}Fe_{0.02}P$ are in good agreement with previous work [2,12].

It is worth noting that the thermal hysteresis of the SCRM-FM transition increases from 20 K for $Mn_{0.98}Fe_{0.02}P$ to as much as 50 K for $Mn_{0.98}Fe_{0.02}P_{0.9}As_{0.1}$, which confirms the first-order nature of the SCR-FM transition [7]. In contrast, the ZFC and FC curves around T_C for the three samples completely overlap, indicating absence of thermal hysteresis. First-order transitions generally show a large change of magnetization around the transition temperature over a small temperature range and consequently have a larger MCE than second-order transitions. However, large thermal hysteresis confines the practical use of the MCE based to the first-order transition [22,23]. Consequently, in this respect, the present $Mn_{0.98}Fe_{0.02}P_{1-x}As_x$ compounds showing a first-order FM-PM transition with no hysteresis may be a good candidate for room-temperature magnetic refrigeration.