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Structural, magnetic properties and magnetocaloric effect of $Mn_{1.2}Fe_{0.8}P_{1-x}Si_xB_{0.03}$ compounds

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ABSTRACT

Structural, magnetic, and magnetocaloric properties of the $Mn_{1.2}Fe_{0.8}P_{1-x}Si_xB_{0.03}$($x$ = 0.4, 0.5 and 0.55) phases have been investigated. The experimental results show that the critical behavior of the paramagnetic to ferromagnetic phase transition can be tuned through the P/Si ratio. An increase in the Si concentration not only raises the Curie temperature from 176 K to 280 K, but also changes the nature of the magnetic transition from the first order (for x = 0.4) to the second order (for x = 0.55) and, thereby, affects the magnetocaloric properties. The peak values of the thermal hysteresis and magnetic entropy change for a magnetic field change of 0–2T are 10 K, 4 K, 0.8 K and −16.3, −8.7, −5.6 J kg^{-1} K^{-1} for x = 0.4, 0.5, and 0.55, respectively. Mechanisms for the magnetic hysteresis loss and possibilities for the room-temperature magnetic refrigeration are discussed.

1. Introduction

Magnetic refrigeration is recognized as an alternative technique to the conventional vapor-cycle cooling due to its higher efficiency and absence of harmful active materials [1–3]. In recent years, a large magnetocaloric effect (MCE) has been found in various intermetallic compounds, such as $Gd_5Si_2Ge_2$, $La(Fe,Si)_{13}$, $MnAs_{1-x}Sb_x$, $MnFeP_{1-x}As_x$, Ni-Mn-In and Gd-based amorphous alloys [4–7]. The $MnFeP_{1-x}As_x$ compounds with the Fe_2P-type structure are of particular interest as they show excellent magnetocaloric properties around room temperature. Because of the arsenic toxicity, many efforts were undertaken to replace As by Ge or Si [8,9]. Full replacement of As by Ge leads to a larger magnetic moment [10], however Ge is too expensive for large-scale applications. The partial or full substitution by Si also yields an enhancement of the MCE, besides it allows tuning the Curie temperature. For $MnFeP_{1-x}Si_x$ system [11], the Si contents of 0.4–0.55 will yield ordering temperatures close to the room temperature (210–330 K). The drawback of $MnFeP_{1-x}Si_x$ is a large thermal hysteresis during the first-order para-to-ferromagnetic phase transition; e.g. the thermal hysteresis reaches ΔT_{hys} = 35 K for the $MnFeP_{0.50}Si_{0.50}$ alloy [12].

A large magnetocaloric effect in the $MnFeP_{1-x}As_x$ and other related phases stems from a first-order magneto-elastic transition (FOMET) [13], during which the crystal structure remains the same but the lattice constants change abruptly across the transition. Thermal hysteresis in these compounds can be decreased by tuning the Mn:Fe ratio. E.g. in the $(Mn,Fe)_{1.95}P_{0.50}Si_{0.50}$ phases, an increase in the Mn:Fe ratio reduces the thermal hysteresis from 5 K to 1 K due to the change from the FOMET to a second-order magnetic transition [14]. However, the magnetic entropy change is also suppressed significantly from 26 J kg^{-1} K^{-1} to 6 J kg^{-1} K^{-1}, which is detrimental for the magnetocaloric cooling. In such cases, one wonders if it is possible to reduce hysteresis while maintaining the first-order magnetostructural transition [15,16]. Recently, it has been reported that addition of B to the Mn–Fe–P–Si alloys might reduce the thermal hysteresis without a penalty to the magnetic entropy change [17]. However, there are no systematic studies on the correlation between the B substitution, P/Si ratio and magnetic properties. Our previous work indicates that the peak magnetic entropy change is achieved at B fraction of 3% in $Mn_{1.15}Fe_{0.85}P_{0.55-x}Si_{0.45}B_x$($x$ = 0.01, 0.03 0.05) compounds. In this paper, it aims to improve MCE and reduce the thermal hysteresis by tuning the P/Si ratio, and to explore effects of the P/Si ratio on the structural, magnetic and magnetocaloric properties of the $Mn_{1.2}Fe_{0.8}P_{1-x}Si_xB_{0.03}$ (x = 0.4, 0.5 and 0.55) compounds.

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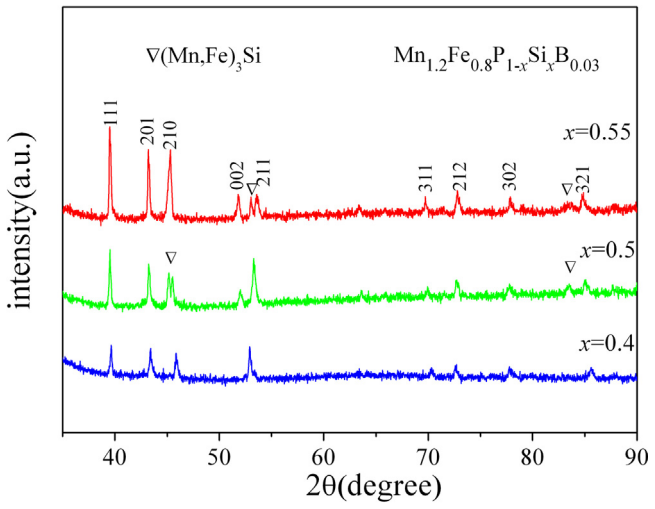

Fig. 1. X-ray diffraction patterns of the $Mn_{1.2}Fe_{0.8}P_{1-x}Si_xB_{0.03}$ compounds with $x = 0.4$, 0.5 and 0.55.

2. Experimental

Polycrystalline $Mn_{1.2}Fe_{0.8}P_{1-x}Si_xB_{0.03}$ samples with $x = 0.4$, 0.5 and 0.55 were synthesized by ball milling. The starting materials were pure Mn powder (purity 99.98%), Fe powder (purity 99.5%), red P powder (purity 99.4%), B powder (purity 99.9%) and Si powder (purity 99.99%). In order to refine the powder particles and improve the composition uniformity, the mixture of the starting materials was firstly ball milled for 5 h in a high-energy vibratory ball mill under Ar atmosphere. The obtained powder mixtures were pressed into pellets and sealed in silica ampoules with Ar gas inside. The pellets were heated at 950 °C for two hours and then slowly cooled down to ambient temperature. Pieces of pellets were then melt-spun into ribbons (with a thickness of about 20–30 μm and a width of 3 mm) on a copper wheel with a speed of 10 m/s using a single-roller melt-spinner in an Ar atmosphere. The obtained ribbons were sealed quartz ampules under 200 mbar of Ar, and then annealed at 1050 °C for 10 min and then quenched in the water. The microstructure and chemical composition of all samples were investigated on a Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) capabilities. The phase purity and crystal structure were verified through X-ray powder diffraction on a PANalytical X'pert Pro MPD instrument, using a monochromatized CuKα_1 radiation (1.54056 Å). The phase analysis and unit cell refinement were done by the Rietveld method, using the Topas 3.0 program. The magnetic data (M vs. T and M vs. H) were measured on a Physical Properties Measurement System (PPMS-9, Quantum Design Co.). The isothermal magnetic entropy change, ΔS_M, was derived from the M vs. H isotherms using the Maxwell equation. The application of the Maxwell relationship to magnetocaloric materials with a first-order phase transition can be cumbersome, but not unfeasible [17]. Use of different measuring protocols can reduce or cancel the appearance of artifacts during the measurements. For materials with a negligible thermal hysteresis, like those in this paper, a spurious spike in the magnetic entropy change may be present when temperature increments between the magnetic isotherms are too small. Therefore, in this work we performed isothermal magnetization measurements with $\Delta T = 5$ K to prevent appearance of artificial peaks.

Table 1
Lattice parameters a and c, unit-cell volume V, and fraction of the $Mn_{1.2}Fe_{0.8}P_{1-x}Si_xB_{0.03}$ ($x = 0.4$, 0.5 and 0.55) compounds.

Material	Fe_2P phase	a(Å)	c(Å)	V(Å^3)	Remark
$x = 0.4$	81%	6.0424	3.4601	109.41	This work
$x = 0.5$	79%	6.0767	3.4286	109.65	This work
$x = 0.55$	78%	6.1008	3.4139	110.04	This work
$Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$	–	6.0836	3.4685(9)	–	[21]
$MnFeP_{0.56}Si_{0.44}$	–	6.022	3.482	–	[11]

3. Results and discussion

The XRD patterns of $Mn_{1.2}Fe_{0.8}P_{1-x}Si_xB_{0.03}$ ($x = 0.4$, 0.5 and 0.55) compounds are shown in Fig. 1. All samples have the major phase of interest with the hexagonal Fe_2P-structure type (JCPDS card No. 88-1803) and a small amount of secondary $(Mn,Fe)_3Si$ phase (space group $Fm3m$, JCPDS card No. 65-3005). For the sample with $x = 0.4$,

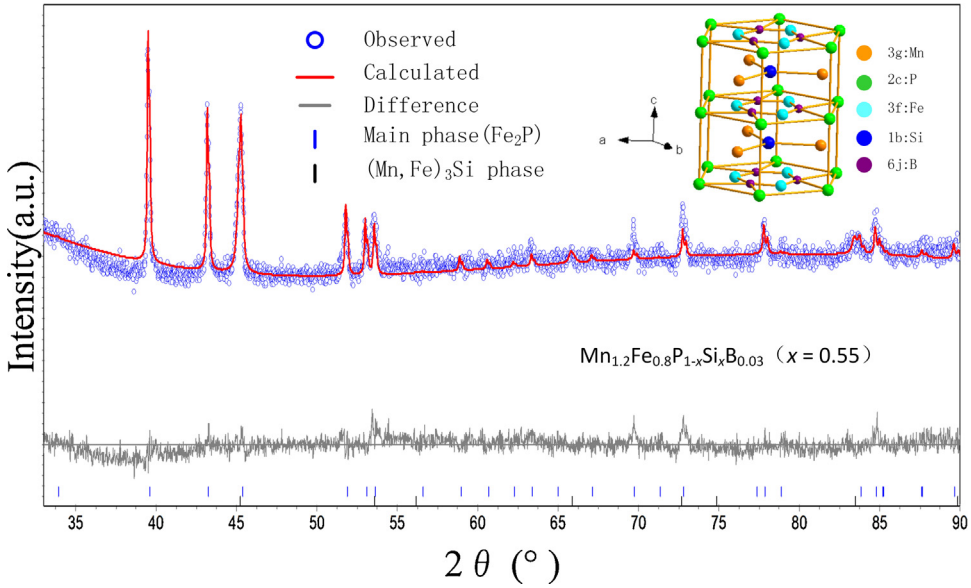

Fig. 2. Observed and calculated XRD patterns of $Mn_{1.2}Fe_{0.8}P_{1-x}Si_xB_{0.03}$ samples with $x = 0.55$. The inset gives the crystal structure of $Mn_{1.2}Fe_{0.8}P_{1-x}Si_xB_{0.03}$ compounds.