Journal of Magnetism and Magnetic Materials 335 (2013) 114–117

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

# Structural, thermal, and magnetic properties of MnFePSiGe compounds prepared by spark plasma sintering method

M. Yue [a,*], H. Xu [a], J.L. Zhao [b], M.F. Xu [a], D.M. Liu [c], J.X. Zhang [a]

[a] College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China
[b] College of Applied Sciences, Beijing University of Technology, Beijing 100124, China
[c] Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing 100124, China

ARTICLE INFO

*Article history:*
Received 10 October 2012
Received in revised form
29 December 2012
Available online 4 February 2013

*Keywords:*
MnFePSiGe compound
$Fe_2P$-type structure
First-order transition

ABSTRACT

Crystal structure, and thermal and magnetic properties have been studied for bulk MnFePSiGe compounds with different silicon contents prepared by the spark plasma sintering method. The MnFePSiGe compounds crystallize in a hexagonal $Fe_2P$-type structure without obvious secondary phase. The compounds undergo a ferromagnetic to paramagnetic first-order transition near their Curie temperature ($T_C$). With increase of Si content, both $T_C$ and magnetic entropy change ($-\Delta S_M$) of the compounds rise remarkably, while the thermal hysteresis ($T_{hys}$) remains almost invariant. For $MnFeP_{0.63}Si_{0.26}Ge_{0.11}$ compound, the $T_C$ and $-\Delta S_M$ for a magnetic field change from 0 to 2 T are 318 K and 27.9 J/Kg K, respectively, and its phase transition entropy change ($\Delta S$) obtained from DSC is 32.3 J/Kg K.



## 1. Introduction

Room temperature magnetic refrigeration based on the magneto-caloric effect (MCE) is considered as one of the most promising technologies to replace vapor-compression refrigeration due to its high-energy efficiency and environmental amity [1]. As a result, many new alloys with giant magneto-caloric effect (GMCE) such as GdSiGe [2], LaFeSi [3], and MnFePAs [4] have been developed. Among these materials, MnFePGe compounds [5,6] have drawn tremendous attention due to their advantages such as excellent magneto-caloric properties, non-toxicity, and low fabrication cost. In our previous study, bulk MnFePGe compounds exhibiting GMCE have been successfully prepared via the spark plasma sintering (SPS) method [7,8]. However, the high cost of Ge is a big concern with respect to practical application. It is therefore necessary to find out a cheaper element to replace some Ge without sacrificing the magneto-caloric properties of the compounds. In the present study, we report on the structural, thermal, and magnetic properties of $MnFeP_{0.89-x}Si_xGe_{0.11}$ compounds with $x=0.14$, 0.18, 0.22, and 0.26.

## 2. Experimental procedure

$MnFeP_{0.89-x}Si_xGe_{0.11}$ compounds with $x=0.14$, 0.18, 0.22, and 0.26 were prepared by mechanical alloying and the subsequent SPS method. Mn powders ( > 99.99 wt %), Fe powders ( > 99.99 wt %), red P powders ( > 99.99 wt %), Ge chips (purity 99.9999%), and Si powders ( > 99.99 wt %) were blended and ball milled for 2 h under Ar atmosphere. The as-milled powders were then collected into a carbon mold and fast consolidated into a $\Phi$ $20\times5$ mm$^2$ cylindrical sample at 1223 K under 30 MPa by the SPS technique. Crystal structure of the as-milled powders and the sintered samples was examined by X-ray diffraction (XRD) with Cu $K\alpha$ radiation. The chemical composition of the sintered samples was analyzed via the inductively coupled plasma (ICP) method. Magnetic measurements were performed in a vibrating sample magnetometer in the temperature interval from 200 to 350 K with a maximum magnetic field of 2 T. Calorimetric measurements were carried out in a TA Instrument DSC Q200 equipped with a Refrigerated Cooling System (RCS).

## 3. Results and discussion

### 3.1. Crystal structure of bulk $MnFeP_{0.89-x}Si_xGe_{0.11}$ compounds

Fig. 1 shows the XRD patterns of the as-milled Mn, Fe, P, Si, and Ge elemental powders with 2 h of ball milling. It is observed that the Si content plays a key role in the formation of MnFePGe compound. In detail, powders with lower Si content ($x=0.14$, 0.18, and 0.22) can crystallize into MnFePSiGe compound possessing $Fe_2P$-type crystal structure with minor impurity of $Fe_2MnSi$ after the ball milling process. As the Si content increases to 0.26, however, the elemental powders fail to combine into the desired

* Corresponding author. Tel.: +86 10 67391760.
*E-mail address:* yueming@bjut.edu.cn (M. Yue).

0304-8853/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jmmm.2013.01.035

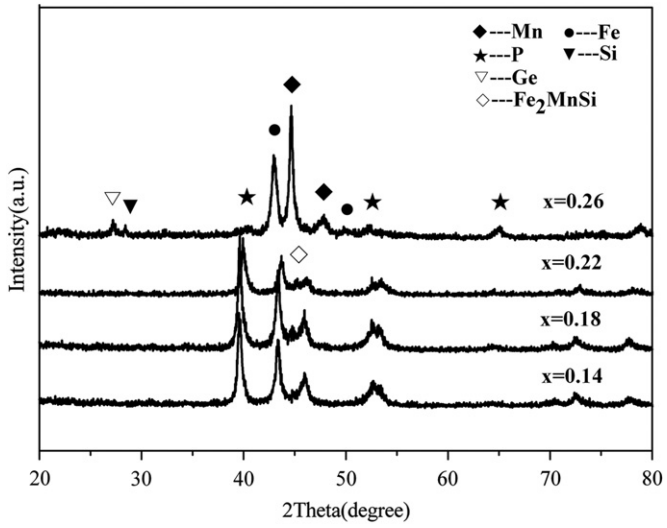


**Fig. 1.** XRD patterns of the as-milled Mn, Fe, P, Si, and Ge elemental powders with ball milling time of 2 h.

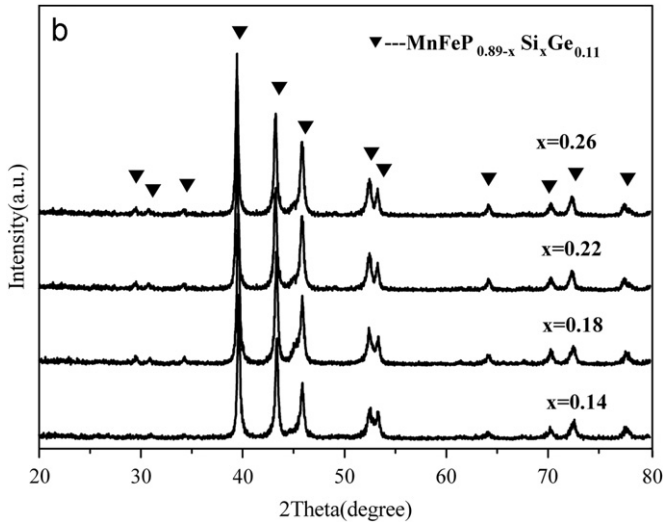


**Fig. 2.** XRD patterns of the bulk $MnFeP_{0.89-x}Si_xGe_{0.11}$ samples ($x=0.14$, 0.18, 0.22, and 0.26) prepared by the SPS method.

compound; they keep the original state instead, indicating that the higher Si content may undermine the solid-state reaction among the elemental powders.

Fig. 2 shows the XRD patterns of the bulk $MnFeP_{0.89-x}Si_xGe_{0.11}$ samples prepared by the SPS method. All the samples possess a hexagonal $Fe_2P$-type crystal structure and the impurity was remarkably removed from the sintered samples. Note that the $MnFeP_{0.63}Si_{0.26}Ge_{0.11}$ sample, which cannot crystallize into $Fe_2P$-type MnFePSiGe compound via ball milling, possesses the desired crystal structure due to the unique plasma-aid sintering process effectively shortening the diffusion paths to ease phase formation and homogenization of the compound. Similar result has been reported in our previous study in MnFePGe compounds [7].

Table 1 shows the crystallographic data of the bulk $MnFeP_{0.89-x}Si_xGe_{0.11}$ compounds. Chemical composition analyses (ICP results) show that the sintered samples more or less preserve the similar composition as the starting powders (nominal composition). For comparison, the nominal and experimental Si contents were listed in the first and second row of the table,

**Table 1**
Crystallographic data of bulk MnFePSiGe compounds as a function of Si content (the first row is the nominal composition, and the second row is the ICP results).

| Si content | Si content | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $c/a$ |
|---|---|---|---|---|---|
| $x=0.14$ | $x=0.141$ | 6.0387 | 3.4716 | 109.32 | 0.5748 |
| $x=0.18$ | $x=0.180$ | 6.0556 | 3.4649 | 110.15 | 0.5722 |
| $x=0.22$ | $x=0.219$ | 6.0748 | 3.4548 | 111.22 | 0.5687 |
| $x=0.26$ | $x=0.260$ | 6.0968 | 3.4501 | 111.81 | 0.5659 |

respectively. As the Si content increases, the $a$ axis lengthens gradually, but the $c$ axis shortens simultaneously, leading to the decrease of the $c/a$ ratio. Meanwhile, the cell volume of the compounds expands due to more replacement of smaller P atom by bigger Si atom.

### 3.2. Thermal properties of bulk $MnFeP_{0.89-x}Si_xGe_{0.11}$ compounds

DSC is an appropriate method to study the thermal properties of first-order phase transitions since it provides a reliable and quantitative way to measure the transition temperature, thermal hysteresis, latent heat, and entropy changes associated with the transition. Fig. 3(a) shows the warming and cooling curves of the bulk $MnFeP_{0.89-x}Si_xGe_{0.11}$ compounds. For every sample, the maximum endothermic peak in the warming curve and the maximum exothermic peak in the cooling curve indicate the temperature of ferromagnetic→paramagnetic and paramagnetic→ferromagnetic phase transition, respectively, and the former temperature was defined as Curie temperature ($T_C$) of the transition. In addition, the temperature difference between the two peaks is the thermal hysteresis ($\Delta T_{hys}$). Derived from Fig. 3(a), the temperature dependence of the entropy for the bulk $MnFeP_{0.89-x}Si_xGe_{0.11}$ compounds upon warming is shown in Fig. 3(b). The starting point and ending point of the transition were marked in every curve; the temperature interval ($\Delta T$) between the two points shows the two-phase coexistence range, which indicates the driving force of the transition process.

Table 2 shows the thermal properties of the bulk $MnFeP_{0.89-x}Si_xGe_{0.11}$ compounds obtained from Fig. 3(a) and (b). As the Si content increases, the $T_C$ increases gradually, while the $\Delta T_{hys}$ decreases simultaneously. Note that the $\Delta T$ increases first, peaks at $x=0.18$ for 13 K, and then decreases again. The variance of $\Delta T$ suggests that the driving force of the ferromagnetic→paramagnetic transition is dependent directly on the Si content in the MnFePSiGe compounds. On the other hand, the entropy change ($\Delta S$) of the transition in MnFePSiGe compounds increases with the increasing Si content in the compounds.

### 3.3. Magnetic properties of bulk $MnFeP_{0.89-x}Si_xGe_{0.11}$ compounds

Fig. 4 shows the temperature dependence of the magnetization of the bulk $MnFeP_{0.89-x}Si_xGe_{0.11}$ compounds. Before measurement, all the samples wrapped with Al foils were put into liquid nitrogen for 2 min and then taken out again; such cooling and heating cycles were performed three times to delete the virgin effect [9]. The obvious thermal hysteresis of the ferromagnetic↔paramagnetic transition upon heating and cooling indicates that the transition of all samples is of the first order, which is usually accompanied with a large magnetic entropy change. The Curie temperature, $T_C$, of all samples was determined from each heating curve where the first temperature derivative of the magnetization has its highest value. The Curie temperature and thermal hysteresis of the bulk $MnFeP_{0.89-x}Si_xGe_{0.11}$ compounds are listed in Table 3. With the increase of Si content, the $T_C$ rises obviously from 252 K for the $MnFeP_{0.75}Si_{0.14}Ge_{0.11}$ compound to