Postprint: Study on Magnetocaloric Properties of Mn1.2Fe0.8P0.74Ge0.26-xSex Compounds

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Abstract

Mn1.2Fe0.8P0.74Ge0.26-xSex (x=0, 0.005, 0.01, 0.015, 0.02, 0.03) compounds were successfully prepared using mechanical alloying (MA) combined with spark plasma sintering (SPS) techniques, and their crystal structure, phase transition processes, and magnetocaloric properties were investigated by means of XRD, DSC, vibrating sample magnetometer (VSM), and direct magnetocaloric effect measurement apparatus. The results indicate that all compounds in this series possess a hexagonal Fe2P structure. With increasing Se content, the lattice constants a and c both undergo significant changes, with c/a first decreasing, then remaining constant, and finally increasing again; moreover, the value of c/a exhibits a certain correspondence with the Tc of the compounds, where a decrease in c/a elevates Tc, and vice versa. Variations in both external magnetic field and temperature can induce a first-order magnetocaloric phase transition in the compounds, i.e., paramagnetic phase (PM) ? ferromagnetic phase (FM). Partial substitution of Ge by Se (x$ $0.015) can enhance the magnetocaloric properties of the material, causing the Curie temperature Tc of the compounds to increase, the transition temperature range ?Tcoex to narrow, and the adiabatic temperature change ?Tad to increase; while the thermal hysteresis ?Thys and entropy change ?SDSC remain essentially unchanged. When x=0.01, the compound exhibits the best magnetocaloric performance and represents a promising room-temperature magnetic refrigeration material; compared with the x=0 compound, Tc is increased by 5.6 K, ?Tcoex is reduced by 10.6%, and ?Tad is increased by 10%; when Se content is further increased, the magnetocaloric properties of the compounds decrease.

Full Text

Research on the Magnetocaloric Properties of $Mn_{1\cdot2}Fe_{0\cdot8}P_{0\cdot74}Ge_{0\cdot26}$ Se Compounds

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ABSTRACT

Magnetic refrigeration based on the magnetocaloric effect offers a potential energy-saving, environmentally friendly alternative to vapor-compression refrigeration. In this work, $Mn_{1\cdot2}Fe_{0\cdot8}P_{0\cdot74}Ge_{0\cdot26}$ Se (x = 0, 0.005, 0.01, 0.015, 0.02, 0.03) compounds were prepared by mechanical milling and subsequent spark plasma sintering (SPS). The crystal structures, phase transition processes, and magnetocaloric properties were investigated using X-ray diffraction (XRD), differential scanning calorimetry (DSC), vibrating sample magnetometry (VSM), and direct measurement equipment for the magnetocaloric effect. The results show that all compounds possess a hexagonal Fe_2P-type crystal structure. With increasing Se concentration, the lattice parameters a and c change significantly, causing the c/a ratio to first decrease, then remain constant, and finally increase again. The Curie temperature (Tc) of the compounds correlates with the c/a ratio: a decrease in c/a raises Tc, while an increase lowers it. Both applied magnetic field and temperature changes can induce a first-order magnetic transition between the paramagnetic (PM) and ferromagnetic (FM) phases.

Low-level substitution of Se for Ge (up to x = 0.015) enhances the magnetocaloric performance, yielding higher Curie temperature, a narrower two-phase coexistence region (ΔTcoex), and larger adiabatic temperature change (ΔTad), while thermal hysteresis (ΔThys) and entropy change (ΔSDSC) remain essentially unaffected. The optimal composition occurs at x = 0.01, which exhibits a 5.6 K increase in Tc, a 10.6% reduction in ΔTcoex, and a 10% increase in ΔTad compared to the Se-free compound. These results demonstrate that MnFePGeSe compounds are promising candidates for room-temperature magnetic refrigeration applications.

KEY WORDS MnFePGeSe, magnetocaloric effect, magnetic phase transition

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1. Introduction

Magnetic refrigeration represents a green and environmentally friendly cooling technology that utilizes magnetocaloric materials as the working substance. This technology offers significant potential for mitigating ozone depletion and

greenhouse effects, thereby protecting the environment and ensuring sustainable human development. Identifying non-polluting, reliable, and highly efficient room-temperature magnetic refrigeration materials is therefore of paramount importance. In recent years, MnFePGe-based compounds have attracted considerable attention due to their excellent magnetocaloric effects and commercial potential. Compared with other room-temperature magnetic refrigeration materials such as GdSiGe, LaFeSi, perovskite-type compounds, and $MnFeP_1$ As , MnFePGe systems offer the advantages of abundant raw materials, low production costs, and environmental friendliness.

For practical magnetic refrigeration applications, materials must exhibit small thermal hysteresis and transition width, large magnetocaloric effects under applied fields below 2 T, and a continuously tunable Curie temperature near room temperature. Previous studies have demonstrated that the magnetic entropy change, Curie temperature (Tc), thermal hysteresis (ΔThys), and transition temperature range (ΔTcoex) in MnFePGe compounds can be tailored by adjusting the Mn/Fe or P/Ge ratios to improve overall performance. Additionally, investigations of Si substitution for Ge, Co/Cr/V/Ti substitution for Fe, and interstitial B addition have yielded important insights for optimizing magnetocaloric properties. Our group' s earlier research on MnFePGe compounds prepared by mechanical alloying (MA) combined with spark plasma sintering (SPS) has shown that this synthesis route produces materials with large magnetic entropy changes.

In this work, we employ MA and SPS techniques to synthesize $Mn_{1\cdot2}Fe_{0\cdot8}P_{0\cdot74}Ge_{0\cdot26}$ Se (x = 0, 0.005, 0.01, 0.015, 0.02, 0.03) compounds, utilizing Se to partially substitute for Ge. This approach is motivated by Se' s comparable atomic radius to Ge and its approximately two-fold lower cost. We systematically investigate the structural and magnetocaloric properties of these materials and elucidate the influence of Se substitution on their performance.

2. Experimental Methods

$Mn_{1\cdot2}Fe_{0\cdot8}P_{0\cdot74}Ge_{0\cdot26}$ Se (x = 0, 0.005, 0.01, 0.015, 0.02, 0.03) compounds were prepared by mechanical alloying and spark plasma sintering. Raw materials consisted of Mn powder (purity ≥ 99.99%), Fe powder (purity ≥ 99.99%), red phosphorus powder (purity ≥ 99.9999%), Ge powder (purity ≥ 99.999%), and Se powder (purity ≥ 99.99%). The synthesis procedure involved: (1) weighing powders according to stoichiometric ratios under Ar atmosphere protection, (2) high-energy ball milling for 1.5 h at 640 rpm using a GN2 mill, (3) loading the milled powder into a 20 mm diameter graphite die, and (4) sintering at 930 °C for 10 min using an SPS-5.40-IV/ET system under a pressure of 30 MPa and vacuum of 6–8 Pa. The samples were furnace-cooled to room temperature after sintering.

Phase composition, crystal structure, and temperature-induced phase transitions were characterized using a Bruker D8 powder X-ray diffractometer (XRD,

Cu Kα). Rietveld refinement was performed using Topas software to determine lattice parameters at 333 K (where compounds are fully paramagnetic). Temperature-dependent XRD data were also analyzed via Rietveld refinement to obtain the integrated intensities of ferromagnetic and paramagnetic peaks, enabling calculation of the paramagnetic phase volume fraction during cooling. Magnetic transition temperatures (Curie temperature, Tc) and entropy changes were measured using a Netzsch 204 F1 differential scanning calorimeter (DSC). Isothermal magnetization curves were obtained with a Quantum Design VersaLab vibrating sample magnetometer (VSM) under magnetic fields up to 3 T, with measurements taken every 3 K during heating. The adiabatic temperature change (ΔTad) was measured directly using equipment developed by the Baotou Rare Earth Research Institute.

3. Experimental Results and Analysis

3.1 Crystal Structure and Phase Composition

Figure 1 [Figure 1: see original paper] presents the XRD patterns of the $Mn_{1·2}Fe_{0·8}P_{0·74}Ge_{0·26}$ Se compounds. All samples exhibit a primary hexagonal Fe_2P-type structure (space group P62m) with trace amounts of MnO and $Ge_6Fe_3Mn_4$ impurities. For compositions with $x \geq 0.015$, minor MnSe secondary phase appears. Table 1 summarizes the lattice parameters at 333 K. While the a lattice parameter shows no systematic variation with Se content, the c parameter initially decreases then increases. This behavior likely arises from the combined effects of ferromagnetic interactions and atomic size effects. Consequently, the c/a ratio first decreases, remains constant, and then increases again. Notably, Tc exhibits a corresponding relationship with c/a: a decreasing c/a ratio elevates Tc, while an increasing ratio suppresses it, and a constant c/a yields an unchanged Tc.

Our previous neutron diffraction studies have determined the atomic positions in MnFePGe compounds: Mn at 3g (x, 0, 1/2), Fe/Mn at 3f (x, 0, 0), P/Ge(1) at 1b (0, 0, 1/2), and P/Ge(2) at 2c (1/3, 2/3, 0). Literature reports based on density functional theory calculations indicate that in Fe_2P-type compounds, substituents larger than P preferentially occupy the 2c site. Furthermore, first-principles calculations show that when substituents occupy the 2c or 1b sites and cause a reduction in c/a, the interlayer ferromagnetic interactions strengthen, leading to higher Curie temperatures. Since Se has a larger atomic radius than P, Se in $Mn_{1·2}Fe_{0·8}P_{0·74}Ge_{0·26}$ Se compounds preferentially occupies the 2c site, thereby reducing c/a and increasing Tc.

3.2 Thermal and Magnetic Properties

DSC measurements were performed to investigate temperature-induced magnetocaloric properties, as shown in Figure 2a [Figure 2: see original paper]. Each sample exhibits distinct endothermic and exothermic peaks during heating and cooling cycles, respectively, with a temperature offset between them, confirm-

ing a first-order magnetic phase transition (FM PM). The endothermic peak temperature corresponds to the Curie temperature (Tc), while the temperature difference between heating and cooling peaks defines the thermal hysteresis (ΔThys). Smaller ΔThys indicates lower thermal losses. The entropy change (ΔSDSC) was calculated from DSC data using the appropriate thermodynamic relationship. Figure 2b shows the temperature dependence of ΔSDSC for x = 0, 0.01, and 0.015 compositions. During heating or cooling, the entropy change increases gradually as the phase transition initiates, rises sharply near Tc, and reaches its maximum upon completion of the transition. The transition temperature range (ΔTcoex), representing the two-phase coexistence region, is defined as the temperature interval between the onset and completion of the transition. Our unpublished results indicate that smaller ΔTcoex values require lower magnetic fields to complete the phase transition, which is advantageous for practical applications.

Table 1 presents the four key magnetocaloric performance parameters—Tc, ΔTcoex, ΔThys, and ΔSDSC—as functions of Se content. As Se content increases, Tc initially rises, then plateaus, and finally decreases, with the maximum Tc of 285.8 K achieved at x = 0.01 (a 5.6 K increase over the Se-free composition). The transition width ΔTcoex shows the opposite trend, reaching a minimum of 7.6 K at x = 0.01, representing a 10.6% reduction. Thermal hysteresis (ΔThys) and entropy change (ΔSDSC) remain relatively constant across compositions, with ΔThys values (maximum 3.2 K) being significantly smaller than those reported for $Mn_{1·2}Fe_{0·8}P_{0·76}Ge_{0·24}$ (ΔThys = 8 K) and $Mn_{1·2}Fe_{0·8}P_{0·75}Ge_{0·25}$ (ΔThys = 4 K). For Se contents exceeding x = 0.015, the magnetocaloric performance deteriorates. Based on comprehensive evaluation of all four parameters, the x = 0 and x = 0.01 compositions exhibit the most promising magnetocaloric properties, warranting further investigation.

3.3 Phase Transition Dynamics

Our previous studies have established that the entropy change in MnFePGe-based magnetocaloric materials directly correlates with the ferromagnetic or paramagnetic phase fraction, where higher ferromagnetic phase content corresponds to larger entropy changes. To investigate the phase transition dynamics, we performed in situ temperature-dependent XRD measurements on $Mn_{1·2}Fe_{0·8}P_{0·74}Ge_{0·26}$ Se (x = 0, 0.01) compounds during cooling from 298 K to 251 K. Figure 3 [Figure 3: see original paper] shows the paramagnetic phase volume fraction as a function of temperature. As temperature decreases, the compounds transform from paramagnetic to ferromagnetic phases, with the paramagnetic fraction decreasing rapidly at first and then more gradually. The rapid transition region spans 283.8–275.0 K for x = 0.01, leaving 23.8% untransformed paramagnetic phase at 275.0 K. For the Se-free composition, the rapid transition occurs between 282.9–268.9 K, with 23.5% paramagnetic phase remaining at 268.9 K. These results indicate comparable entropy changes but a narrower transition width for the Se-doped material, consistent with the DSC

results.

3.4 Magnetic Field-Induced Properties

Isothermal magnetization curves for x = 0 and x = 0.01 compositions are presented in Figure 4 [Figure 4: see original paper]. The magnetization approaches saturation with increasing magnetic field, with lower temperatures requiring smaller fields to reach saturation. This behavior confirms that both magnetic field and temperature can induce the magnetic phase transition. The magnetic entropy change (ΔSM) was calculated from these curves using the Maxwell relation. Figure 5 [Figure 5: see original paper] shows the resulting ΔSM(T) curves for magnetic field changes of 0–1 T, 0–2 T, and 0–3 T. Under a 3 T field, the x = 0.01 composition exhibits a maximum ΔSM of 18.6 J/(kg · K) at its Tc of 285.8 K, while the Se-free composition shows a maximum of 17.6 J/(kg · K) at 280.2 K. Thus, Se substitution slightly increases the magnetic entropy change while significantly raising Tc. The field-induced entropy changes are somewhat lower than the temperature-induced values from DSC (Table 1), likely because the applied magnetic field is insufficient to complete the full phase transition. The magnetic entropy change increases more substantially between 1–2 T than between 2–3 T, indicating that most of the transition occurs below 2 T, with only minor additional transformation at higher fields. This behavior mirrors the temperature-induced transition and may be attributed to difficulty in transforming small crystallites.

Direct measurements of the adiabatic temperature change (ΔTad) for x = 0 and x = 0.01 compositions are shown in Figure 6 [Figure 6: see original paper] for a 1.5 T field change. Both compounds exhibit maximum ΔTad values near their respective Tc values: 2.0 K for x = 0 and 2.2 K for x = 0.01, representing a 10% improvement. This enhancement likely stems from the reduced ΔTcoex, which lowers the magnetic field required to complete the phase transition.

4. Conclusions

1. $Mn_{1·2}Fe_{0·8}P_{0·74}Ge_{0·26}$ Se (x = 0, 0.005, 0.01, 0.015, 0.02, 0.03) compounds were rapidly synthesized via mechanical alloying combined with spark plasma sintering. All compounds crystallize in the hexagonal Fe_2P structure (space group P62m) with minimal secondary phases. With increasing Se content, the lattice parameters a and c exhibit significant changes, causing the c/a ratio to first decrease, then remain constant, and finally increase. The c/a ratio correlates directly with Tc: decreasing c/a elevates Tc, while increasing c/a suppresses it.

2. Both temperature and applied magnetic field can induce a first-order magnetic phase transition (PM FM) in $Mn_{1·2}Fe_{0·8}P_{0·74}Ge_{0·26}$ Se compounds. The transition proceeds rapidly at first and then slows with decreasing temperature or increasing magnetic field.

3. Partial substitution of Se for Ge enhances the magnetocaloric performance of $Mn_{1\cdot2}Fe_{0\cdot8}P_{0\cdot74}Ge_{0\cdot26}$ Se compounds by increasing the Curie temperature, narrowing the transition width (ΔTcoex), and enlarging the adiabatic temperature change (ΔTad), while thermal hysteresis (ΔThys) and entropy change (ΔSDSC) remain essentially unchanged. The optimal composition, x = 0.01, exhibits a 5.6 K increase in Tc, a 10.6% reduction in ΔTcoex, and a 10% increase in ΔTad compared to the undoped compound, making it highly promising for practical applications. Magnetocaloric performance degrades for Se contents exceeding x = 0.015.

References

[1] Cam Thanh D T, Brück E, Tegus O, Klaasse J C P, Gortenmulder T J, Buschow K H J. J Appl Phys, 2006; 99: 08Q107
[2] Yan A, Müller K H, Schultz L, Gutfleisch O. J Appl Phys, 2006; 99: 08K903
[3] Dagula W, Tegus O, Fuquan B, Zhang L, Si P Z, Zhang M, Zhang W S, Brück E, de Boer F R, Buschow K H J. IEEE Trans Magn, 2005; 41: 2778
[4] Ou Z Q, Wang G F, Lin S, Tegus O, Brück E, Buschow K H J. J Phys: Condens Matter, 2006; 18: 11577
[5] Tegus O, Fuquan B, Dagula W, Zhang L, Brück E, Si P Z, de Boer F R, Buschow K H J. J Alloys Compd, 2005; 396: 6
[6] Yue M, Li Z Q, Wang X L, Liu D M, Zhang J X, Liu X B. J Appl Phys, 2009; 105: 07A915
[7] Pecharsky V K, Gschneidner K A. Phys Rev Lett, 1997; 78: 4494
[8] Hu F X, Shen B G, Sun J R. Appl Phys Lett, 2001; 78: 3675
[9] Chen W, Zhong W. J Funct Mater, 1998; 29: 236
[10] Tegus O, Bruck E, Buschow K H J, de Boer F R. Nature, 2002; 415: 150
[11] Tegus O, Brück E, Li X W, Zhang L, Dagula W, de Boer F R, Buschow K H J. J Magn Magn Mater, 2004; 272: 2389
[12] Brück E, Kamarad J, Sechovsky V, Arnold Z, Tegus O, de Boer F R. J Magn Magn Mater, 2007; 310: e1008
[13] Trung N T, Qu Z Q, Gortenmulder T J, Tegus O, Buschow K H J, Brück E. Appl Phys Lett, 2009; 94: 102513
[14] Wang G F, Song L, Li F A, Ha S C L, Li X W, Tegus O. Acta Metall Sin, 2008; 43: 889
[15] Geng Y X, Tegus O. J Magn Mater Devices, 2011; 42: 17
[16] Ha S C L, Ning J, He X L, Yi R L T, Song L, Tegus O, Huang J H. J Magn Mater Devices, 2010; 41: 24
[17] Liu Y J, Geng Y X, Tegus O, Ha S C L, Song Z Q, Hai S, Li S. J Inner Mongolia Normal Univ, 2012; 41: 368
[18] Wang D M, Song L, Wang Y H, Zhang W, Geng Y X, Tegus O. Rare Met, 2012; 36: 87
[19] Wang D M, Song L, Wang Y H, Zhang W, Bi L G, Tegus O. Acta Metall Sin, 2011; 47: 344
[20] Liu D M, Huang Q Z, Yue M, Lynn J W, Liu L J, Chen Y, Wu Z H, Zhang J X. Phys Rev, 2009; 80B: 174415

[21] Liu D M, Yue M, Zhang J X, McQueen T M, Lynn J W, Wang X L, Chen Y, Li J Y, Cava R J, Liu X B, Altounian Z, Huang Q. Phys Rev, 2009; 79B: 014435
[22] Gercsi Z, Delczeg-Czirjak E K, Vitos L, Wills A S, Daoud-Aladine A, Sandeman K G. Phys Rev, 2013; 88B: 024417
[23] Delczeg-Czirjak E K, Gercsi Z, Bergqvist L, Eriksson O, Szunyogh L, Nordblad P, Johansson B, Vitos L. Phys Rev, 2012; 85B: 094433
[24] Xu H, Yue M, Zhao C, Zhang D T, Zhang J X. Rare Met, 2012; 31: 336
[25] Zhang L, Liu D M, Deng X J, Yue M, Zhang J X. J Funct Mater, 2011; 42: 1951
[26] Yue M, Liu D M, Huang Q Z, Wang T, Hu F X, Li J B, Rao G H, Shen B G, Lynn J W, Zhang J X. J Appl Phys, 2013; 113: 17A902
[27] Zhang M, Liu D M, Liu C X, Huang Q Z, Wang S B, Zhang H, Yue M. Acta Metall Sin, 2013; 49: 783
[28] Liu L J. Master Thesis, Beijing University of Technology, 2009

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