Magnetocaloric Properties of (MnFeRu)\textsubscript{2}(PSi) as Magnetic Refrigerants near Room Temperature

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Abstract: We have scaled up the production process of magnetic refrigerants near room temperature. The \(\text{Mn}_x\text{Fe}_y\text{Ru}_{1-x}\text{P}_{1-y}\text{Si}_z\) compounds with \(0.03 \leq x \leq 0.16\), \(y = 0.75\), and \(z = 0.55\) were synthesized and their magnetocaloric properties were examined. By changing the compositions and the annealing temperature, the Curie temperature was tuned between 275 and 315 K with 2–3 K steps. All the compounds underwent a first-order magnetic transition accompanied by thermal hysteresis of less than 2 K. The compounds showed excellent magnetocaloric properties: the magnetic entropy change was more than 10 J/K·kg and the refrigerant capacity was about 115 J/kg in a field change of 1.5 T. The detailed instructions to synthesize high-performance (MnFe)\textsubscript{2}PSi materials are given.

Keywords: magnetocaloric effect; magnetic refrigeration; first-order magnetic transition; magnetic entropy

1. Introduction

About 40 years ago, Brown reported the first demonstration of magnetic cooling near room temperature [1]. Since then, considerable effort has been devoted to developing magnetic refrigeration systems. Magnetic refrigeration is based on magnetocaloric effects (MCEs), which mean changing the entropy or temperature of magnetic materials by applying/removing the magnetic field. Since this technology is environmentally friendly and highly energy-efficient, magnetic refrigeration is expected to be an alternative cooling technology to conventional gas compression systems in the near future. To realize magnetic refrigeration systems, materials exhibiting large MCEs are strongly desired. Some ferromagnetic materials are known to undergo a first-order magnetic transition (FOMT) at the Curie temperature, \(T_C\), and show giant MCEs near room temperature. Typical examples are Gd\textsubscript{3}Si\textsubscript{2}Ge\textsubscript{2} [2], MnAs\textsubscript{3}Sb\textsubscript{5} [3], MnFeP\textsubscript{1−y}As\textsubscript{y} [4], La(Fe\textsubscript{1−x}Si\textsubscript{x})\textsubscript{3}H\textsubscript{y} [5], and NiMnSn Heusler alloys [6]. These materials are potential candidates for magnetic refrigerators. Note that, except Gd\textsubscript{3}Si\textsubscript{2}Ge\textsubscript{2}, these candidates are 3d transition metal-based compounds. Among them, Mn\textsubscript{2−y}Fe\textsubscript{y}P\textsubscript{1−z}Si\textsubscript{z}, which is a derivative system of MnFeP\textsubscript{1−z}As\textsubscript{z}, is one of the most promising materials near room temperature, because it consists of nontoxic and inexpensive elements and the compound is very stable in water as well as in air. This system has a hexagonal Fe:P-type structure in the concentration ranges of \(0 \leq y \leq 1\) and \(0.28 \leq z \leq 0.64\). The structure has two chemical sites for transition metals, 3g and 3f. Neutron diffraction studies have revealed that Mn atoms preferentially occupy the 3g site, while Fe atoms occupy the 3f site [7]. In 2008, Cam Thanh et al. succeeded in preparing Mn\textsubscript{2−y}Fe\textsubscript{y}P\textsubscript{1−z}Si\textsubscript{z} with the Fe:P-type structure for the first time [8]. They found that the compounds with \(y = 1\) and \(z \approx 1\) undergo a FOMT and exhibit giant MCEs near room temperature. However, these compounds
have a large thermal hysteresis, $\Delta T_{hyp}$, of 20–30 K, which is unfavorable for magnetic refrigeration materials. Subsequent work reported that heat treatment does not improve the hysteretic behavior [9]. Therefore, it is necessary to change the compositions or to dope guest elements for the reduction of $\Delta T_{hyp}$ without losing the giant MCEs. Dung et al. successfully reduced $\Delta T_{hyp}$ by choosing $y = 0.7$–0.8 [10]. On the other hand, we reported that the Ru substitution in $\text{Mn}_x\text{Fe}_y\text{P}_z\text{Si}$ is effective to reduce $\Delta T_{hyp}$ [11]. A similar doping effect was also reported for Co and Ni substitutions [12]. One of the advantages of the Ru-substituted system is the moderate change of $T_C$ with the Ru content. We have shown that $T_C$ of the materials can be tuned to the desired temperature by changing the Ru content.

For practical applications, it is important to develop the production process at an industrial scale. For this purpose, we constructed an electric furnace, the tube of which is made of stainless steel with a diameter of 100 mm [13]. This furnace enables us to synthesize plate-type materials up to 250 g and rod-type materials up to 700 g in one batch. In this paper, we report the magnetic phase transitions and MCEs of $\text{Mn}_x\text{Fe}_y\text{Ru}_z\text{P}_1\text{Si}$ with $0.03 \leq x \leq 0.16$, $y = 0.75$, and $z = 0.55$ produced at an industrial scale. We have established a recipe to synthesize giant magnetocaloric materials, which have the Curie temperature of 275–315 K with 2–3 K steps.

2. Results and Discussion

We prepared a number of samples with different compositions and different heat treatments to tune $T_C$ to 275–315 K. In this paper, we show the results of 14 samples, the compositions and sintering temperature of which are listed in Table 1. Some of them have the same compositions and the sintering temperature is different. As described in Section 3, the samples were annealed after sintering to ensure homogeneity. We found that repetitive annealing is effective to make the FOMT sharper.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Nominal Composition</th>
<th>Sintering Temp. (°C)</th>
<th>$T_C$ (K)</th>
<th>$\Delta T_{hyp}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn$<em>{1.24}$Fe$</em>{0.86}$Ru$<em>{0.14}$P$</em>{0.46}$Si$_{0.54}$</td>
<td>1105</td>
<td>280.4</td>
<td>1.4</td>
</tr>
<tr>
<td>2</td>
<td>Mn$<em>{1.24}$Fe$</em>{0.86}$Ru$<em>{0.14}$P$</em>{0.46}$Si$_{0.54}$</td>
<td>1110</td>
<td>284.5</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>Mn$<em>{1.24}$Fe$</em>{0.84}$Ru$<em>{0.12}$P$</em>{0.46}$Si$_{0.54}$</td>
<td>1105</td>
<td>288.1</td>
<td>1.4</td>
</tr>
<tr>
<td>4</td>
<td>Mn$<em>{1.24}$Fe$</em>{0.84}$Ru$<em>{0.12}$P$</em>{0.46}$Si$_{0.54}$</td>
<td>1100</td>
<td>289.7</td>
<td>1.8</td>
</tr>
<tr>
<td>5</td>
<td>Mn$<em>{1.23}$Fe$</em>{0.86}$Ru$<em>{0.12}$P$</em>{0.46}$Si$_{0.54}$</td>
<td>1100</td>
<td>292.3</td>
<td>1.7</td>
</tr>
<tr>
<td>6</td>
<td>Mn$<em>{1.23}$Fe$</em>{0.87}$Ru$<em>{0.10}$P$</em>{0.46}$Si$_{0.54}$</td>
<td>1100</td>
<td>294.3</td>
<td>1.5</td>
</tr>
<tr>
<td>7</td>
<td>Mn$<em>{1.24}$Fe$</em>{0.86}$Ru$<em>{0.08}$P$</em>{0.46}$Si$_{0.54}$</td>
<td>1100</td>
<td>296.1</td>
<td>1.8</td>
</tr>
<tr>
<td>8</td>
<td>Mn$<em>{1.24}$Fe$</em>{0.86}$Ru$<em>{0.08}$P$</em>{0.46}$Si$_{0.54}$</td>
<td>1095</td>
<td>297.4</td>
<td>1.7</td>
</tr>
<tr>
<td>9</td>
<td>Mn$<em>{1.24}$Fe$</em>{0.86}$Ru$<em>{0.08}$P$</em>{0.46}$Si$_{0.54}$</td>
<td>1090</td>
<td>299.7</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>Mn$<em>{1.23}$Fe$</em>{0.78}$Ru$<em>{0.05}$P$</em>{0.46}$Si$_{0.54}$</td>
<td>1100</td>
<td>302.3</td>
<td>1.8</td>
</tr>
<tr>
<td>11</td>
<td>Mn$<em>{1.23}$Fe$</em>{0.70}$Ru$<em>{0.05}$P$</em>{0.46}$Si$_{0.54}$</td>
<td>1090</td>
<td>305.3</td>
<td>1.7</td>
</tr>
<tr>
<td>12</td>
<td>Mn$<em>{1.23}$Fe$</em>{0.71}$Ru$<em>{0.04}$P$</em>{0.46}$Si$_{0.55}$</td>
<td>1085</td>
<td>309.0</td>
<td>1.8</td>
</tr>
<tr>
<td>13</td>
<td>Mn$<em>{1.23}$Fe$</em>{0.71}$Ru$<em>{0.04}$P$</em>{0.46}$Si$_{0.55}$</td>
<td>1090</td>
<td>311.8</td>
<td>1.8</td>
</tr>
<tr>
<td>14</td>
<td>Mn$<em>{1.23}$Fe$</em>{0.72}$Ru$<em>{0.03}$P$</em>{0.46}$Si$_{0.55}$</td>
<td>1085</td>
<td>315.9</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 1a,b illustrate the DSC curves of Mn$_{1.24}$Fe$_{0.76}$Ru$_{0.08}$P$_{0.46}$Si$_{0.54}$. The numbers in the figure represent the sample numbers in Table 1. The solid lines are the data for the samples annealed twice and the dashed lines are for the samples annealed once. It was seen that the second annealing increased the peak height for all the samples by 10%–30%. This means that repetitive annealing improves homogeneity and it makes the magnetic transition sharper. The DSC peak position is close to the Curie temperature. The peak temperature slightly changed with additional annealing. The temperature interval between the two adjacent DSC peaks was 2–4 K. As listed in Table 1, samples 7, 8, and 9 have the same compositions. We found that the higher sintering temperature decreased $T_C$. A similar tendency was also observed for the other sample sets with the same compositions. Recently,
Yu et al. reported the effects of heat treatment on the structure and magnetic properties of Mn$_{1.15}$Fe$_{0.85}$P$_{0.52}$Si$_{0.45}$B$_{0.03}$ [14]. They found that $T_C$ increases with increasing the annealing temperature, which is contrary to our cases. These results suggest that the annealing temperature has a strong impact on the composition of the main phase with the FeP-type structure. Höglén et al. studied the phase diagram of FeMnP$_{1-x}$Si$_x$ and found that three phases coexist in the concentration range of 0.50 ≤ $x$ ≤ 1.0: the hexagonal FeP-type phase, the hexagonal MnSi$_x$-type phase and the cubic FeSi-type phase [15]. It is likely that selective diffusion between the main phase and the impurity phases or grain boundaries is responsible for the different dependence of $T_C$ on the annealing temperature. To clarify this problem, further metallurgical studies are necessary. Our results indicate that adjusting the annealing temperature is effective to control the Curie temperature in the present system.

![Figure 1](image1.png)

**Figure 1.** Differential scanning calorimetry (DSC) curves of (a) samples No. 1–7 and (b) samples No. 8–14. The numbers represent the sample numbers listed in Table 1. The solid lines represent the DSC curves measured for the samples annealed twice and the dashed lines are those for the samples annealed once. All the curves are measured in the heating process.

Figure 2 displays the temperature dependence of the magnetization of the selected samples at a magnetic field of 1 T. Both the heating and cooling processes are plotted. All the compounds undergo a FOMT accompanied by thermal hysteresis. The Curie temperature was obtained from the peak position of $dM/dT$ vs. $T$ curves at 0.2 T in the heating process, which is also listed in Table 1. The Ru concentration dependence of the $T_C$ of three series, Mn$_{1.25}$Fe$_{0.75}$–Ru$_x$P$_{0.46}$Si$_{0.54}$, Mn$_{1.25}$Fe$_{0.75}$–Ru$_x$P$_{0.45}$Si$_{0.55}$, and Mn$_{1.25}$Fe$_{0.75}$–Ru$_x$P$_{0.46}$Si$_{0.55}$, is depicted in Figure 3. In the figure, different $T_C$ values of the same compositions, which depend on the annealing temperature, are also shown. Since the differences in Mn/Fe and P/Si contents between the three series were trivial, the Curie temperature was mainly determined by the Ru content. Roughly speaking, $T_C$ decreased with increasing the Ru content linearly at a rate of 2.5 K/at. % Ru. This value was much smaller than that of the Co substitution (4.3–6.6 K/at. % Co) or Fe substitution (5.6–8.1 K/at. % Ni) for (MnFe)$_{1-x}$P$_{0.5}$Si$_{0.5}$ [16]. In this sense, the Ru-substituted system is advantageous for the fine control of $T_C$ by changing the content. The thermal hysteresis estimated from Figure 2 is listed in Table 1. All the compounds have a $\Delta T_{hyst}$ less than 2 K. Figure 4a,b show the temperature dependence of the magnetic entropy change of Mn$_{1.22}$Fe$_{0.78}$–Ru$_x$P$_{0.46}$Si$_{0.54}$ in a field change of 1.5 T. Most of the samples had peak values of the magnetic entropy change, $\Delta S_{mag}$, higher than 10 J/K·kg. The $\Delta S_{mag}$ of samples 5, 8 and 9 exceeded 15 J/K·kg. The half width of the $\Delta S_M$ peak was in the range of 4–7 K. On the other hand, the difference in $T_C$ between the adjacent sample numbers was, at most, 4 K (see Table 1). Thus, a large overlap of two adjacent $\Delta S_M$ vs. $T$ curves was observed between the $\Delta S_M$ peaks. This means that the temperature range from 280 to 320 K was completely covered by Mn$_{1.22}$Fe$_{0.78}$–Ru$_x$P$_{0.46}$Si$_{0.54}$ with large MCEs, which is critical for magnetic refrigerators.
Figure 2. Temperature dependence of magnetization of selected Mn$_{1.24}$Fe$_{0.76-x}$Ru$_x$P$_{0.46}$Si$_{0.54}$ compounds in a magnetic field of 1 T. The numbers represent the sample numbers listed in Table 1. Both heating and cooling processes are plotted.

Figure 3. Ru concentration dependence of $T_c$ of three Mn$_{1.24}$Fe$_{0.76-x}$Ru$_x$P$_{0.46}$Si$_{0.54}$ series. The Curie temperature was estimated from the peak position of $dM/dT$ – $T$ curves at 0.2 T in the heating process.

Figure 4. Temperature dependence of the magnetic entropy change of (a) samples No. 1–7 and (b) samples No. 8–14 in field changes of 1.5 T. The numbers represent the sample numbers listed in Table 1. The data were obtained in the heating process.

We calculate the refrigerant capacity of the samples, $q$, from the following equation,
where $2\delta T$ is the temperature interval of integration. In the present study, we used $2\delta T = 30$ K. The calculated $q$ values in a field change of 1.5 T are illustrated in Figure 5 by red circles as a function of $T_c$. Except for a few samples, the $q$ of Mn$_{1.24}$Fe$_{0.76}$Ru$_{0.46}$P$_{0.54}$Si$_{0.54}$ was about 115 J/kg. This value is about 1.4 times as large as that of metallic Gd in the same temperature interval. These results also demonstrate the excellent magnetocaloric properties of the Ru-substituted (MnFe)$_2$PSi compounds. In Figure 5, the $\Delta S_{\text{max}}$ values are also plotted by blue squares. In contrast to $q$, $\Delta S_{\text{max}}$ shows a broad maximum in the $T_c$ dependence.

![Figure 5](image-url)

**Figure 5.** The refrigerant capacity, $q$, (red circles) at 1.5 T and the peak values of the magnetic entropy change, $\Delta S_{\text{max}}$, (blue squares) at 1.5 T of Mn$_{1.24}$Fe$_{0.76}$Ru$_{0.46}$P$_{0.54}$Si$_{0.54}$ plotted as a function of the Curie temperature. Dashed lines are guides to the eye.

This is understood as follows. From the Maxwell relation, $\Delta S_M$ is expressed as:

$$\Delta S_M = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH.$$  \hspace{1cm} (2)

Therefore, sharp FOMTs give large $\Delta S_{\text{max}}$. As the Curie temperature is raised, the magnetic transition becomes less sharp, because the system approaches the critical boundary for the FOMT. This causes a decrease in $\Delta S_{\text{max}}$ with the increasing $T_c$. On the other hand, the magnetic transition becomes broad with the increasing the Ru content, because Ru is a nonmagnetic element. Then, lowering $T_c$ gives rise to a reduction of $\Delta S_{\text{max}}$, and, as a result, $\Delta S_{\text{max}}$ has a maximum at an intermediate $T_c$. When the magnetic transition is round, the half width of the $\Delta S_M$ peak becomes large. Consequently, the refrigerant capacity is constant in the whole temperature range studied.

### 3. Materials and Methods

The samples were synthesized in the standard procedures: (1) mixing in a ball mill, (2) sintering in the furnace, (3) pulverizing at room temperature, and (4) subsequent annealing. The purity of the raw materials are 3 N for Mn, Fe, and Ru, 4 N for Si, and 6 N for P. Metallic powders and small pieces of P and Si weighted in desired compositions were mixed in a planetary ball mill under Ar atmosphere. The ball milling was carried out for 10 h at a rotational speed of 200 rpm using hardened stainless steel vials and balls. The resultant was placed in a carbon boat and sintered in a furnace for 5 h. The inside of our furnace tube can be evacuated. Sintering was done under Ar atmosphere. After cooled down to room temperature, the products were pulverized and mixed in a ball mill. Then, the samples were annealed at the same temperature as sintering for 5 h to ensure homogeneity. The procedures (3) and (4) were repeated to improve homogeneity. The amount of one batch is about
70 g in this study. X-ray diffraction measurements were carried out for some samples. The diffraction patterns indicate that the samples have an almost single phase with the Fe₃P-type structure. Very weak peaks due to the impurity phase with the cubic FeSi-type structure were detected. No differences between the X-ray diffraction patterns of the same compositions with different annealing temperature were observed. The differential scanning calorimetry (DSC) measurements were performed using a commercial DSC apparatus, DSC7000X (Hitachi High-Tech Science, Tokyo, Japan) with heating rate of 2 K/min in the temperature range of 243–328 K. The magnetization was measured in a commercial SQUID magnetometer, MPMS-5S (Quantum Design Japan, Tokyo, Japan). The magnetic entropy change, $\Delta S_m$ is obtained from the Maxwell relation given in Equation (2). It is important to note that $\Delta S_m$ is sometimes overestimated by applying the $M - H$ data to the Maxwell relation, when the material has large thermal hysteresis. This is because some parts of the sample remain in the ferromagnetic state, when a magnetic field is removed at a temperature around $T_c$. Consequently, both the ferromagnetic and paramagnetic states coexist and the material shows an anomalous $M - H$ curve at an adjacent temperature, giving rise to incorrect $\Delta S_m$. Detailed discussion on this problem is given in the literature [17–19]. In the present study, the $M - T$ curves measured at various fields are used to estimate $\Delta S_m$. Our group confirmed that this method gives correct $\Delta S_m$ [20,21]. The sample was cooled down far below $T_c$ in zero field and the $M - T$ curve was recorded in the heating process.

4. Conclusions

We have studied the magnetocaloric properties of Mn$_{1.24}$Fe$_{0.76}$–Ru$_x$P$_{0.4}$Si$_{0.54}$ compounds with $0.03 \leq x \leq 0.16$ and obtained the following conclusions.

(i) Repetitive annealing improves the homogeneity of the sample and it makes the magnetic transition sharper.

(ii) We succeeded in the fine control of $T_c$ between 275 and 315 K by changing the Ru content and the sintering temperature. Roughly speaking, $T_c$ is determined by the Ru content and it is decreased by increasing the Ru content nearly linearly at a rate of 2.5 K/at. % Ru in Mn$_{1.24}$Fe$_{0.76}$–Ru$_x$P$_{0.4}$Si$_{0.54}$.

(iii) All the compounds undergo the FOMT and exhibit large MCEs with $\Delta T_{fb}$ less than 2 K. It was found that the refrigerant capacity is almost constant in the composition ranges studied.

These results indicate that Mn$_{1.24}$Fe$_{0.76}$–Ru$_x$P$_{0.4}$Si$_{0.54}$ compounds are excellent candidates for magnetic refrigerants near room temperature.

Finally, we add supplementary comments on our production process. In the present study, the samples were synthesized by sintering and annealing. This method is advantageous for the production of a large amount of materials at an industrial scale compared with other methods, such as melt spinning or the drop synthesis method. The amount of one sample is about 70 g, which is larger than that prepared by using quartz ampoules in a laboratory. Our samples underwent a sharper FOMT than those synthesized in quartz ampoules. Moreover, we confirmed that the Curie temperature is reproducible within ±1 K when the samples are prepared with the same initial compositions and the same annealing temperature [13]. These results demonstrate that our method gives homogeneous and reliable materials.

Recent magnetic refrigeration systems are based on the active magnetic regenerator (AMR) cycle. In this cycle, a large temperature span can be achieved by adopting the layered structure of several materials. The present study indicates that the Mn$_{1.24}$Fe$_{0.76}$–Ru$_x$P$_{0.4}$Si$_{0.54}$ system offers a large temperature span from 275 K to 315 K. To test the cooling power, we are mounting the present compounds to the magnetic refrigeration system. The results will be reported in the near future.

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Author Contributions: Keiichiro Yamashita designed the experiments. Takayuki Ohnishi and Kei Soejima performed the experiments. Hiroyuki Wada analyzed the experimental data. All of the authors contributed to discussion and Hirofumi Wada wrote the manuscript.
Conflicts of Interest: The authors declare no conflict of interest.

References


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