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DOI
10.1016/j.jallcom.2019.06.239

Publication date
2019

Document Version
Final published version

Published in
Journal of Alloys and Compounds

Citation (APA)
Lai, J., Huang, B., Miao, X., Van Thang, N., You, X., Maschek, M., ... Brück, E. (2019). Combined effect of annealing temperature and vanadium substitution for mangetocaloric Mn\(_{1.2-x}V_x\)Fe\(_{0.75}P_{0.5}Si_{0.5}\) alloys. Journal of Alloys and Compounds, 803, 671-677. https://doi.org/10.1016/j.jallcom.2019.06.239

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Combined effect of annealing temperature and vanadium substitution for mangetocaloric Mn$_{1.2-x}$V$_x$Fe$_{0.75}$P$_{0.5}$Si$_{0.5}$ alloys

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A R T I C L E   I N F O

Article info
Received 4 March 2019
Received in revised form 12 June 2019
Accepted 18 June 2019
Available online 20 June 2019

Keywords:
Mn, V, Fe$_{1.05}$(P, Si)
Neutron diffraction
Magnetocaloric
Magnetic properties
Entropy

A B S T R A C T

Approaching the border of the first order transition and second order transition is significant to optimize the giant magnetocaloric materials performance. The influence of vanadium substitution in the Mn$_{1.2-x}$V$_x$Fe$_{0.75}$P$_{0.5}$Si$_{0.5}$ alloys is investigated for annealing temperatures of 1323, 1373 and 1423 K. By tuning both the annealing temperature and the V substitution simultaneously, the magnetocaloric effect can be enhanced without enlarging the thermal hysteresis near the border of the first to second order transition. Neutron diffraction measurements reveal the changes of site occupation and interatomic distances caused by varying the annealing temperature and V substitution. The properties of the alloy with $x = 0.02$ annealed at 1323 K is comparable to those found for the MnFe$_{0.95}$P$_{0.595}$Si$_{0.330}$B$_{0.075}$ alloy, illustrating that Mn$_{1.2-x}$V$_x$Fe$_{0.75}$P$_{0.5}$Si$_{0.5}$ alloys are excellent materials for magnetic heat-pumping near room temperature.

1. Introduction

Recently, near room temperature magnetic heat-pumping technology has attracted broad attention due to its high efficiency, low impact on the environment, low noise, and long service life compared with the conventional vapor-compression technology [1]. The giant magnetocaloric effect (GMCE) materials, which are utilized as active regenerator, form a key factor to determine the efficiency of this technology, GMCE occurs in some materials that undergo a first-order magnetic transition (FOMT), such as Gd$_2$Ge$_2$Si$_2$ [2], LaFe$_{12-x}$Si$_x$ [3-5], MnFeP$_{1-x-y}$Si$_y$B$_y$ [6-8], MnCoGe$_x$ [9] and Heusler [10] alloys. Among them, the MnFeP$_{1-x-y}$Si$_y$B$_y$ alloys are currently regarded as one of the most promising materials that can be industrialized because of their cheap and non-toxic elements, high cooling capacity and tunable $T_C$ near room temperature [7]. Nevertheless, thermal hysteresis ($\Delta T_{hys}$) in MnFeP$_{1-x-y}$Si$_y$B$_y$ alloys still limits their application since it lowers the efficiency of the cooling cycle. Lots of research has been done to reduce $\Delta T_{hys}$ while maintaining the GMCE. In order to obtain a limited $\Delta T_{hys}$, the compositions can be tuned to shift the FOMT towards the border with a second-order magnetic phase transition (SOMT), as demonstrated for MnFeP$_{1-x-y}$Si$_y$B$_y$ [11] or for the transition metal substitution in Mn$_{1.5}$Co$_x$Fe$_{0.95}$P$_{0.5}$Si$_{0.5}$ and MnFe$_{0.95}$Ni$_{0.05}$P$_{0.5}$Si$_{0.5}$ [12]. Additionally, $\Delta T_{hys}$ can also be controlled by the annealing time and temperature. For example, in Mn$_{1.15}$Fe$_{0.85}$P$_{0.53}$Si$_{0.45}$ alloys [13], $\Delta T_{hys}$ decreases with the annealing temperature. The effect of the annealing temperature and time on the magnetic phase transition of Mn$_{1.00}$Fe$_{0.950}$P$_{0.595}$Si$_{0.330}$B$_{0.075}$ alloys have been investigated [14] and the annealing temperature was found to show a strong influence on $\Delta T_{hys}$. Mn$_{1.2}$Fe$_{0.75}$P$_{0.5}$Si$_{0.5}$ alloys [15] annealed at 1373 K in a two-step heat treatment process were reported to have a strong FOMT with a relatively low $\Delta T_{hys}$ of 5 K.

However, the combined effect of the annealing temperature and...
element substitutions has not been studied yet. Sintering of Mn-Fe-P-Si alloys can be regarded as a solid-state diffusion process as the annealing temperature is below the melting point (1553 K). The diffusion rate of each element strongly depends on the annealing temperature. Therefore, introducing extra elements in the Mn-Fe-P-Si alloy requires a different annealing temperature. Here we report the combined effect of a changing annealing temperature (1323, 1373 and 1423 K) and V substitution ($x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05$) in $\text{Mn}_{1.2-x}\text{V}_x\text{Fe}_{0.75}\text{P}_{0.5}\text{Si}_{0.5}$ alloys, resulting in a change in the hexagonal crystal structure and the magnetic properties. The substitution of Mn by V can be controlled by adjusting the annealing temperature in order to approach the border of the FOMT and SOMT.

2. Experimental

Polycrystalline $\text{Mn}_{1.2-x}\text{V}_x\text{Fe}_{0.75}\text{P}_{0.5}\text{Si}_{0.5}$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05$) alloys were prepared by powder metallurgy. The starting materials Mn (99.7%), Fe (99.7%), red P (99%), Si (99.7%) and V (99.5%) powders were mechanically ball milled in a PULVERISETTE 7 planetary mill for 10 h in an Ar atmosphere with a constant rotation speed of 380 rpm, and finally sealed in quartz ampoules under 200 mbar of Ar. These tablets were then annealed at 1323, 1373 and 1423 K for 2 h in order to promote crystallization and slowly cooled down to room temperature. Subsequently, they were heated up to the same annealing temperature for 20 h to homogenize and quenched in water.

The X-ray diffraction (XRD) patterns were collected on a PANalytical X-pert Pro diffractometer with Cu-Kα radiation (1.54056 Å) at room temperature (RT). The room-temperature neutron diffraction data were collected at a wavelength of 1.67105 Å on the neutron powder diffraction instrument PEARL [16] at the research reactor of Delft University of Technology. The crystal structures and atom occupancies were refined using the Rietveld refinement method implemented in the Fullprof software package [17,18]. The temperature and magnetic field dependence of the magnetization was measured by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS 5XL) in the reciprocating sample option (RSO) mode. The adiabatic temperature change ($\Delta T_{ad}$) is measured in a Peltier cell based DSC using a Halbach cylinder magnetic field ($\leq 1.5$ T). In this setup, the isofield calorimetric scans were performed at a rate of 3.0 K/min, while the temperature lag due to the thermal resistance of the Peltier cells has been corrected.

3. Results and discussions

The magnetization as a function of the temperature for $\text{Mn}_{1.2-x}\text{V}_x\text{Fe}_{0.75}\text{P}_{0.5}\text{Si}_{0.5}$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04$ and 0.05) alloys after annealing at 1323, 1373 and 1423 K is shown in Fig. 1. The values are extracted from isofield measurements (decreasing from 2 to 0.2 T in steps of 0.2 T) to ensure that thermal history effects are removed. The ferromagnetic - to - paramagnetic transition temperature $T_C$ is determined by the corresponding temperature where a maximum is observed in the $|dM/dT|$ curves. $T_C$ tends to decrease with increasing V substitution after annealing at 1323, 1373 and 1423 K, as shown in Fig. 1 (d). For the alloys annealed at 1373 K, $T_C$ deviates from the linearity in the $x = 0.02$, in which the sample shows a higher low field MCE, see Fig. 4 (b). $T_C$ is sensitive to

![Fig. 1](image-url)
changes in internal structure or internal symmetry [19]. The observed changes are in good agreement with the trends for the $c/a$ ratio in the refined lattice parameters (see Fig. 2(d)).

The thermal hysteresis $\Delta T_{\text{hys}}$ is defined as the difference in $T_C$ for the heating and cooling process, which will hinder the efficiency of the magnetic cooling [20]. It is important to minimize $\Delta T_{\text{hys}}$ while maintaining a sufficient GMCE. In this work, $\Delta T_{\text{hys}}$ is determined by the difference in the transition temperature during heating and cooling in a field of 1 T. The values of $T_C$, $\Delta T_{\text{hys}}$ and latent heat ($L$) for the Mn$_{1.2-x}$V$_x$Fe$_{0.75}$P$_{0.5}$Si$_{0.5}$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05$) alloys after annealing at 1323, 1373 and 1423 K are shown in Table 1. Since materials with a pronounced FOMT usually show large $L$ values [21], the values of $L$ can be regarded as a sign of the strength of the FOMT. In general, V substitutions for Mn can reduce both $\Delta T_{\text{hys}}$ and $L$. When $x$ increases from 0.00 to 0.05, $\Delta T_{\text{hys}}$ decreases dramatically from 12.8 K to 1.4 K for annealing at 1423 K, while it decrease from 2.1 K to below the experimental resolution for annealing at 1323 K. Note that the limited $\Delta T_{\text{hys}}$ for the Mn$_{1.2-x}$V$_x$Fe$_{0.75}$P$_{0.5}$Si$_{0.5}$ alloys annealed at 1323 K is promising for practical applications. For the alloy with $x = 0.02$ the values of $\Delta T_{\text{hys}}$ and $L$ are unexpectedly larger than those for $x = 0.01$ for annealing at 1323 and 1373 K, which suggests a stronger first-order transition. As shown in Table 2, the increase in occupation of Fe on the 3$f$ site may contribute to a strengthened FOMT.

Rietveld refinement of room-temperature XRD data shows that, in the Mn$_{1.2-x}$V$_x$Fe$_{0.75}$P$_{0.5}$Si$_{0.5}$ alloys, the hexagonal Fe$_2$P-type phase (space group $P-62m$) corresponds to the main phase and a MnFe$_2$Si-type phase (space group F$m3m$) is found as impurity phase [22]. The impurity phase fraction for each annealing temperature (see Fig. 2) is roughly at the same level for $x \leq 0.04$, which allows for an independent comparison of the effects of V substitution on the alloys annealed at the same annealing temperature. For the alloys with $x \leq 0.03$ annealed at 1323 and 1373 K, the impurity phase fraction is around 8.0 ± 1.0 vol%. When the annealing temperature rises to 1423 K, the impurity increases to around 11.5 ± 0.5 vol%. These results indicate that a large impurity phase-fraction will be introduced at a higher annealing temperature. The higher fraction of impurity can be one of the reasons for the

![Fig. 2. Relationship between the (a–c) lattice parameters $a$ and $c$, (d) $c/a$, and (e) the phase fraction of impurity phase and the V content of Mn$_{1.2-x}$V$_x$Fe$_{0.75}$P$_{0.5}$Si$_{0.5}$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05$) alloys after annealing at 1323, 1373 and 1423 K.]
larger $\Delta T_{\text{hys}}$ as was proposed by Gutierrez et al. [23].

From crystal structure refinement (summarized in Fig. 2), we observe trends for the lattice parameter change as a function of V concentration, which are similar for all the three annealing temperatures: the $a$ axis decreases and the $c$ axis increases, leading to an increase in $c/a$ ratio. The deviation of lattice parameters from linearity is related to the fluctuation of impurity since the 3.1 phase of impurity affects the metallic and non-metalllic ratio in the Fe$_2$P-type, see Fig. 2(e). The amplitude of the change varies according to the annealing temperature. For $x = 0.05$, the change in $c/a$ ratio is 1.0, 0.5 and 0.4% at an annealing temperature of 1323, 1373 and 1423 K, respectively. There is a smaller change at higher annealing temperatures, which may be caused by some segregation into the inter-grain secondary phase, as can be seen in Fig. 2(e).

In the Mn-rich Mn-Fe-P-Si alloy, it is reported that the Fe atoms preferentially occupy the 3$f$ site, the Mn atoms the 3$g$ site, the P atoms and Si atoms the 2$c$ or 1$b$ sites randomly [24]. X-ray absorption and powder diffraction experiments combined with density functional theory (DFT) calculations revealed that an electronic redistribution takes place in Mn-Fe-P-Si-R, which is at the origin of the giant entropy change and results in a large change in the electron density for Fe on the 3$f$ site and the surrounding Si/P atoms. [25].

Additionally, first-principles calculations suggest that larger magnetic moments will develop on the 3$f$ and 3$g$ sites when there are more coplanar Si nearest neighbors [26]. In order to investigate the relationship between the site occupancies and the magneto-elastic phase transition, it is significant to investigate both the atom positions and the site occupation in the Fe$_2$P-type structure. As shown in Table 2, the P and Si atoms occupy the 2$c$ and 1$b$ site randomly and the 3$g$ site is fully occupied by Mn, which is consistent with a previous study [25]. Note that, the occupation of Fe on the 3$f$ site increases when the annealing temperature increases.

Table 1

<table>
<thead>
<tr>
<th>$x$</th>
<th>Annealed at 1423 K</th>
<th>Annealed at 1373 K</th>
<th>Annealed at 1323 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>$\Delta T_{\text{hys}}$ (K)</td>
<td>$L$ (kJ/kg)</td>
</tr>
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<td>256.4</td>
<td>12.8</td>
<td>7.6</td>
</tr>
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<td>250.5</td>
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</tr>
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<td>9.1</td>
<td>5.9</td>
</tr>
<tr>
<td>0.03</td>
<td>230.4</td>
<td>5.4</td>
<td>5.6</td>
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<td>215.3</td>
<td>3.8</td>
<td>4.5</td>
</tr>
<tr>
<td>0.05</td>
<td>212.5</td>
<td>1.4</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 2

The site occupation of the 3$f$, 3$g$, and 2$c$ sites for the Mn$_{1.2}$Fe$_{0.75}$P$_{0.5}$Si$_{0.5}$ alloys annealed at 1323, 1373 and 1423 K. The site occupation of the 3$g$ site is less in comparison with a previous study [25]. Note that, the occupation of Fe on the 3$f$ site increases when the annealing temperature increases. The sample with $x = 0.02$ has a smaller $a$ axis and a larger $c$-axis compared to the one without V.

In the Fe$_2$P-type structure, the magneto-elastic coupling originates from so-called mixed magnetism: the Mn/(Fe(3$g$)) value for a field change of 1 T than the sample with $x = 0$ (see Fig. 4(b)). This is probably due to an enhanced magnetic coupling caused by V on the 3$f$ site (shown in Table 2). Fig. 3(b) shows the lattice parameters calculated from the neutron diffraction patterns, which are consistent with results from XRD patterns. The $c$-axis decreases and the $a$-axis increases when increasing the annealing temperature. The sample with $x = 0.02$ has a smaller $a$ axis and a larger $c$-axis compared to the one without V.

To investigate the site preference for V in the Fe$_2$P-type structure, refinements have been conducted assuming that V is (i) all located exclusively on the 3$f$ site, (ii) located exclusively on the 3$g$ site or (iii) randomly distributed over the 3$f$ and 3$g$ sites, resulting in $\chi^2$ values of 5.16, 16.4 and 5.19, respectively. From these results it is concluded that V has a slight preference to occupy the 3$f$ site.

For the alloys annealed at 1373 K, the sample $x = 0.02$ has a larger $\Delta S_M$ value for a field change of 1 T than the sample with $x = 0$ (see Fig. 4(b)). This is probably due to an enhanced magnetic coupling caused by V on the 3$f$ site (shown in Table 2). Fig. 3(b) shows the lattice parameters calculated from the neutron diffraction patterns, which are consistent with results from XRD patterns. The $c$-axis decreases and the $a$-axis increases when increasing the annealing temperature. The sample with $x = 0.02$ has a smaller $a$ axis and a larger $c$-axis compared to the one without V.

In the Fe$_2$P-type structure, the magneto-elastic coupling originates from so-called mixed magnetism: the Mn/(Fe(3$g$)) value for a field change of 1 T than the sample with $x = 0$ (see Fig. 4(b)). This is probably due to an enhanced magnetic coupling caused by V on the 3$f$ site (shown in Table 2). Fig. 3(b) shows the lattice parameters calculated from the neutron diffraction patterns, which are consistent with results from XRD patterns. The $c$-axis decreases and the $a$-axis increases when increasing the annealing temperature. The sample with $x = 0.02$ has a smaller $a$ axis and a larger $c$-axis compared to the one without V.
of interlayer Mn (3g) - Mn/Fe (3f) has no notable change when increasing the annealing temperature. However, the distance of interlayer Mn (3g)-Mn/Fe (3f) that has 4 bonds in neighbor (the diamond symbols) increases, shown in Fig. 3 (c). These competitions weakens the magnetic exchange interaction in the Mn(3g) site and results in a decrease in the transition temperature \( T_C \). Compared to the alloy without V annealed at 1373 K, the Mn\(_{1.18}\)V\(_{0.02}\)Fe\(_{0.75}\)P\(_{0.5}\)Si\(_{0.5}\) alloy annealed at 1373 K (open symbols) has a larger distance of both the intra layer Mn (3g)-P/Si (1b) and Mn (3g)-Mn (3g). This shrinkage in the plane (z = 0.5) can explain the decreases in \( T_C \) induced by the V substitution.

The iso-field magnetization curves of annealed Mn\(_{1.2-x}\)V\(_x\)Fe\(_{0.75}\)P\(_{0.5}\)Si\(_{0.5}\) (\( x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05 \)) for a magnetic field change of 0–2 T are measured in the vicinity of \( T_C \) at temperature intervals of 1 K. The \( \Delta S_M \) values of the alloys is derived from extracted isothermal magnetization curves based on the Maxwell relation [28,30].

Temperature dependence of \( \Delta S_M \) for a field change of 0–1 T (open symbols) and 0–2 T (solid symbols) for Mn\(_{1.2-x}\)V\(_x\)Fe\(_{0.75}\)P\(_{0.5}\)Si\(_{0.5}\) (\( x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05 \)) alloys after annealing at 1323, 1373 and 1423 K are shown in Fig. 4 (a), (b) and (c), respectively. With increasing annealing temperatures, \( \Delta S_M \) increases and \( T_C \) decreases, which agrees with the previous report on the effect of annealing temperature for MnFe\(_{0.95}\)P\(_{0.5}\)Si\(_{0.33}\)B\(_{0.075}\) alloys [14,15]. On the other hand, for increasing V substitutions, \( \Delta S_M \) decreases and \( T_C \) decreases. The alloy with \( x = 0.02 \) annealed at 1373 K even has a larger \( \Delta S_M \) value (18.4 J/(kg K)) than that with \( x = 0.00 \) (17.2 J/(kg K)) under an external field of 1 T. For a field change of 0–2 T, these two samples have equal values of \( \Delta S_M \). This indicates that the alloy with 0.02 at% has better low-field (1 T) performance.

Since 1 T is the magnetic field applied in current heat pump prototypes with low-cost NdFeB permanent magnets, it is very significant to have high performance under this field. The current alloys with \( x = 0.00 \) annealed at 1323 K (\( \Delta S_M = 8.2 \) J/(kg K)) at 282 K for a field change of 0–1 T with \( \Delta T_{DSC} = 2.1 \) K is comparable to the boron doping alloys such as the MnFe\(_{0.95}\)P\(_{0.5}\)Si\(_{0.33}\)B\(_{0.075}\) alloys annealed at 1323 K (\( \Delta S_M = 6.2 \) J/(kg K)) at 285 K for a field change of 0–1 T and the MnFe\(_{0.95}\)P\(_{0.5}\)Si\(_{0.33}\)B\(_{0.077}\) alloys annealed at 1373 K [9] (\( \Delta S_M = 9.8 \) J/(kg K)) at 281 K with \( \Delta T_{DSC} = 1.6 \) K. These results suggest that both a decreasing annealing temperature and an increasing V substitution can tune the strong first-order magnetic transition to the boundary between the first-order to second-order magnetic transition in the Mn\(_{1.2}\)Fe\(_{0.75}\)P\(_{0.5}\)Si\(_{0.5}\) alloys. Fig. 5 (a) illustrates the temperature dependence of the value of in-field DSC of \( T_{DSC} \) for several Mn\(_{1.2-x}\)V\(_x\)Fe\(_{0.75}\)P\(_{0.5}\)Si\(_{0.5}\) alloys annealed at 1323 K, while Fig. 5 (b) illustrates the temperature dependence of \( \Delta T_{DSC} \) for Mn\(_{1.2-x}\)V\(_x\)Fe\(_{0.75}\)P\(_{0.5}\)Si\(_{0.5}\) alloys annealed at 1373 K. The value of \( \Delta T_{DSC} \) is determined by using the following equation [31].

\[
\Delta T_{DSC} = T \frac{C_P(H)}{\Delta S_M(H)}
\]

where \( C_P(H) \) is the specific heat. Note that there are two peaks in the vicinity of \( T_C \) for the sample \( x = 0.00 \). This is in line with previous observations as two different Fe\(_2\)P-type phases with close compositions have been reported to co-exist if annealing is preferred at relative lower temperatures [14]. When \( x \) increases from 0.00 to 0.02 for the sample annealed at 1323 K, the values of...
$\Delta T_{ad}$ increases from 1.8 to 2.7 K and $|\Delta S_M|$ decrease from 8.2 to 7.6 J kg$^{-1}$ K$^{-1}$ under an external field change of 1 T. Compared to the alloy without V, a significant $\Delta T_{ad}$ of 2.7 K for a field change of 1 T and a limited hysteresis (1.8 K) are achieved in the alloy with $x = 0.02$ annealed at 1323 K, indicating that it is a promising candidate for magnetic heat-pumping.

For the sample annealed at 1373 K, the values of $\Delta T_{ad}$ increases from 3.3 to 4.8 K for an external field change of 1 T by increasing $x$ from 0.00 to 0.02. The intermediate hysteresis in these samples is about 4.5 K. Note that it is important to distinguish the value of $\Delta T_{ad}$ from the cyclic (direct) field-induced temperature changes ($\Delta T_{cyclic}$) in first order materials showing a large hysteresis. $\Delta T_{cyclic}$ reflects the practical working situation of the magnetic heat-pumping, while the $\Delta T_{ad}$ reflects the potential [12]. For the materials with a large hysteresis, $\Delta T_{ad}$ turns out to be much higher than $\Delta T_{cyclic}$. Thus, it is concluded that V substitution can increase $\Delta T_{ad}$ when annealed at 1323 and 1373 K.

Thus, it is concluded that V substitution can increase $\Delta T_{ad}$ when annealed at 1323 and 1373 K.

4. Conclusions

By decreasing the annealing temperature and increasing V substitution for Mn, it is possible to tune the strong first-order magnetic transition to the boundary between the first-order to second-order magnetic transition. Increasing the V substitution brings a decrease in the $a$-axis and an increase on the $c$-axis. As a result, $T_C$ decreases. V has shown a preference to occupy the $3f$ site and shortens the interatomic distance. Compared to V free sample, the alloy with $x = 0.02$ has a better magnetocaloric effect in a low magnetic field change of 1 T when annealing at 1323 and 1373 K. The competitive low-field performance promotes the application...
of low-cost NdFeB permanent magnets. A larger temperature change $\Delta T_{\text{eff}}$ of 2.7 K and a low hysteresis of 1.8 K are achieved by optimizing the alloy with $x = 0.02$ annealed at 1323 K, which is comparable to the MnFe$_{0.95}$P$_{0.595}$Si$_{0.33}$B$_{0.075}$ alloy. Mn$_{1.2-x}$V$_{x}$Fe$_{0.75}$P$_{0.5}$Si$_{0.5}$ alloys can therefore become a promising material for magnetic heat-pumping near room temperature.

Acknowledgements

The authors acknowledge Anton Lefering, Kees Goubitz, and Bert Zwart for their technical assistance and Dr. Yibole and Dr. Maurits Boeije for discussion. This work has been financially supported by the Dutch national research organization NWO TTW. This work is also supported by Guangdong Provincial Science and Technology Program (Grant No. 2015A050502015), the Guangzhou Municipal Science and Technology Program (No. 201707010056), the Natural Science Foundation of Guangdong Province (2016A030313494, 2018A030313615, 2018A030310406). The author thanks the Guangzhou Ethics Project for finance support.

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