Effects of the Substitution of 20% Nd for La or Doping with 20% C on the Magnetic Properties and Magnetocaloric Effect in LaFe$_{11.5}$Si$_{1.5}$ Compound

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Abstract: The effects of element substitution and element doping on the magnetic properties and magnetocaloric effect of the LaFe$_{11.5}$Si$_{1.5}$ compound were investigated. The crystals of the LaFe$_{11.5}$Si$_{1.5}$, La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$, and LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ compounds all showed cubic NaZn$_{13}$-type structures, but the lattice of the La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$ shrunk and the lattice of the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ expanded. All three compounds had the characteristic of first-order magnetic transition due to the obvious itinerant-electron metamagnetic (IEM) transition occurring above Curie temperature ($T_C$). For the LaFe$_{11.5}$Si$_{1.5}$, La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$, and LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ compounds, the $T_C$ were approximately 194 K, 188 K, and 232 K, respectively. Meanwhile, the maximum magnetic entropy changes ($-\Delta S_M$) under a magnetic field change of 0–3 T were approximately 18.7 J/kg K, 22.8 J/kg K, and 16.4 J/kg K, respectively. The $T_C$ was mainly affected by the lattice constant. Furthermore, the $-\Delta S_M$ was mainly affected by the latent heat of the first-order magnetic transition.

Keywords: La(Fe,Si)$_{13}$ compounds; Curie temperature; magnetic transition; magnetocaloric effect

1. Introduction

Recently, room-temperature magnetic refrigeration technology based on the magnetocaloric effect (MCE) has attracted extensive attention due to its significant advantages, such as its high efficiency, its energy saving, non-toxic and pollution-free qualities, its simple and compact structure, and its low noise [1–6]. This technology is expected to be used in devices that produce energy-efficient coatings.

The LaFe$_{11.3-x}$Si$_x$ ($1.2 \leq x \leq 1.6$) compound has become one of the preferred materials for magnetic refrigeration technology due to its large magnetocaloric effect, low cost, and environmental protection. Its refrigeration capacity depends on the temperature-induced ferromagnetic-paramagnetic transition and the magnetic-field-induced itinerant-electron metamagnetic (IEM) transition of NaZn$_{13}$-type main phase near the Curie temperature ($T_C$). However, the $T_C$ of the compound is between 190 K and 250 K. It is difficult to meet the refrigeration demand at room temperature [7–10].

At present, the $T_C$ of LaFe$_{11.3-x}$Si$_x$ compound is regulated mainly by replacing part of the La with rare-earth elements [11,12], and by replacing part of the Fe with transition-metal elements [13,14], doping interstitial atoms [15,16], etc. For example, Fujieda et al. [17] found that the lattice constant $a$ and $T_C$ gradually decreased with increasing Pr content in the La$_{11-x}$Pr$_x$(Fe$_{0.88}$Si$_{0.12}$)$_3$ compound. When $x = 0$, $a = 1.468$ nm and $T_C = 195$ K. Meanwhile, when $x = 0.5$, $a = 1.446$ nm and $T_C = 186$ K. Hu et al. [18] found that when $x$ was taken as 0.04, 0.06, and 0.08, the $T_C$ of La(Fe$_{1-x}$Co$_x$)$_{11.5}$Si$_{1.5}$ were 243, 274, and 301 K, respectively. The ferromagnetic ordering was accompanied by a negative lattice expansion. Balli et al. [19] found that the insertion of 1.3 nitrogen atoms per LaFe$_{11.7}$Si$_{1.3}$ formula (i.e., the formation
of LaFe\textsubscript{11.7}Si\textsubscript{1.3}N\textsubscript{1.3}) can increase the lattice parameter and \(T_C\) from 11.467 to 11.733 Å and from 190 to ~230 K, respectively. However, the differences in magnetic properties caused by the different regulation methods have not been systematically compared. In this work, the effects of element substitution and element doping on magnetic properties and magnetocaloric effects are compared. For simplicity, the aim of the element substitution scheme is to replace 20% La with Nd in the LaFe\textsubscript{11.5}Si\textsubscript{1.5} compound (i.e., to form a La\textsubscript{0.8}Nd\textsubscript{0.2}Fe\textsubscript{11.5}Si\textsubscript{1.5} compound). Meanwhile, the aim of the element-doping scheme is to introduce interstitial C with an atomic coefficient ratio of 20% in the LaFe\textsubscript{11.5}Si\textsubscript{1.5} compound (i.e., to form the LaFe\textsubscript{11.5}Si\textsubscript{1.5}C\textsubscript{0.2} compound). This provides an experimental and theoretical basis for the application of the LaFe\textsubscript{13−x}Si\textsubscript{x} compound.

2. Experimental Procedure

The samples of nominal compositions of LaFe\textsubscript{11.5}Si\textsubscript{1.5}, La\textsubscript{0.8}Nd\textsubscript{0.2}Fe\textsubscript{11.5}Si\textsubscript{1.5}, and LaFe\textsubscript{11.5}Si\textsubscript{1.5}C\textsubscript{0.2} were prepared by arc-melting appropriate amounts of the raw materials of La (99.5% in purity), Nd (99.9% in purity), Fe (99.9% in purity), Si (99.999% in purity), and Fe-C alloy (carbon content: 3.5 wt.%) under a high-purity argon atmosphere. The obtained samples were repeatedly melted several times to ensure homogeneity. Each sample was approximately 100 g. The samples were subsequently sealed in a quartz tube under high vacuum. An annealing treatment at 1393 K for 20 days in a muffle furnace (NJ11-KBF-16Q-V, Zhongxi Huada Technology Co., Ltd., Beijing, China) was carried out; subsequently, the samples were quenched in liquid nitrogen. Finally, the powdered samples were obtained for subsequent testing.

A powder X-ray diffraction (XRD; D8-Advance, Bruker, Karlsruhe, Germany) was performed by using Cu Ka radiation at room temperature to identify the crystal structure and crystal lattice constants. A vibrating sample magnetometer (VSM; 7410, LakeShore, Westerville, OH, USA) was used to measure the thermomagnetic curves under an external magnetic field of 0.01 T and isothermal magnetization curves under an external magnetic field change of 0–3 T. The VSM-7410 is currently the most sensitive vibrating sample magnetometer in the world, and it can guarantee at least \(5 \times 10^{-7}\) emu. The isothermal magnetic entropy change (\(-\Delta S\)) was obtained according to the Maxwell relation [20]:

\[
\Delta S(T, H) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH
\]  

3. Results and Discussion

The XRD patterns of the LaFe\textsubscript{11.5}Si\textsubscript{1.5}, La\textsubscript{0.8}Nd\textsubscript{0.2}Fe\textsubscript{11.5}Si\textsubscript{1.5}, and LaFe\textsubscript{11.5}Si\textsubscript{1.5}C\textsubscript{0.2} are shown in Figure 1. According to the comparison with the PDF card in Jade software, all these samples were crystallized in a single phase with a cubic NaZn\textsubscript{13}-type structure (the space group is \textit{Fm-3c}). Compared with the LaFe\textsubscript{11.5}Si\textsubscript{1.5}, the fact that the Nd had a smaller atomic radius than the La may have caused the lattice shrinkage in the La\textsubscript{0.8}Nd\textsubscript{0.2}Fe\textsubscript{11.5}Si\textsubscript{1.5} and its XRD diffraction peaks to move to a slightly higher angle. Furthermore, the introduction of interstitial C atoms may have caused the lattice expansion in the LaFe\textsubscript{11.5}Si\textsubscript{1.5}C\textsubscript{0.2} and its XRD diffraction peaks to move to a slightly lower angle. By using Jade software, the XRD data were refined to obtain the lattice constants. The lattice constants of the LaFe\textsubscript{11.5}Si\textsubscript{1.5}, La\textsubscript{0.8}Nd\textsubscript{0.2}Fe\textsubscript{11.5}Si\textsubscript{1.5}, and LaFe\textsubscript{11.5}Si\textsubscript{1.5}C\textsubscript{0.2} were approximately 11.475 Å, 11.462 Å, and 11.484 Å, respectively. The different lattice constants could prove the shrinkage or expansion of the afore-mentioned lattices.
The substitution of the La by the Nd with a smaller atomic radius may have led to the value in the heating process [21]. The Fe-Fe bond length and weakening the Fe-Fe exchange interaction, resulting in a lower Tc. Moreover, the introduction of interstitial C in the LaFe 11.5Si1.5 may have increased the number of 3d electrons, resulting in a higher Tc. Correspondingly, the introduction of interstitial C in the LaFe11.5Si1.5 may have increased the number of 3d electrons, resulting in a higher Tc. (2) The Tc is closely related to the Fe-Fe bond length, especially the Fe(8b)-Fe(96i) bond length [23]. The substitution of the La by the Nd with a smaller atomic radius may have led to the lattice shrinkage, thus reducing the Fe-Fe bond length and weakening the Fe-Fe exchange interaction, resulting in a lower Tc. Correspondingly, the introduction of interstitial C may have led to the lattice expansion, thus increasing the Fe-Fe bond length and enhancing the Fe-Fe exchange interaction, resulting in a higher Tc. Moreover, the M-T curves of each sample show obvious thermal hysteresis. The thermal hysteresis can be estimated from the difference in the temperature of the magnetic transition between cooling and heating, and it is evidence of the first-order magnetic transition of materials. The thermal hysteresis of the LaFe11.5Si1.5, La0.8Nd0.2Fe11.5Si1.5, and LaFe11.5Si1.5C0.2 were approximately 2.8, 4.3, and 1.3 K, respectively.
Figure 2. Temperature dependence of magnetization for LaFe$_{11.5}$Si$_{1.5}$, La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$, and LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ under an external magnetic field of 0.01 T.

The isothermal magnetization curves (i.e., $M$–$H$ curves) of the LaFe$_{11.5}$Si$_{1.5}$, La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$, and LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ measured in a wide temperature range under an external magnetic field change of 0–3 T are shown in Figure 3. For the temperature range measured in Figure 3, the temperature step is 2 K in the vicinity of $T_C$ and 5 K for the range far away from $T_C$. For all the samples, at temperatures well below $T_C$, the magnetization increased rapidly with the increasing magnetic field and approached saturation at lower magnetic fields. At temperatures well above $T_C$, an approximately linear relationship between the magnetization and the magnetic field can be observed. It is noteworthy that all the samples underwent a magnetic-field-induced IEM transition from the paramagnetic state to the ferromagnetic state at temperatures slightly higher than $T_C$. For the magnetic hysteresis, the La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$ was the most obvious, the LaFe$_{11.5}$Si$_{1.5}$ was the second, and the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ was the weakest. The greater magnetic hysteresis was not conducive to the effective refrigerating efficiency of the samples [11].

In addition, for the three compounds, since the magnetic transition was accompanied by a sudden change in the unit-cell volume (magnetoelastic coupling), there was latent heat in the phase transition during the magnetic transition. The appearance of thermal hysteresis and magnetic hysteresis in the $M$–$T$ and $M$–$H$ curves further proves that these three compounds are typical first-order magnetic transition materials.

The Arrott plots of the LaFe$_{11.5}$Si$_{1.5}$, La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$, and LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ are shown in Figure 4. According to studies on the Landau theory and Arrott plots [24], the phase transition properties can be inferred from the Arrott plot near the $T_C$. The fourth-order coefficient of the Landau free-energy expansion is negative when the metamagnetic transition behavior occurs, which is manifested by the appearance of an inflection point or a negative slope on the Arrott plot [21,25]. Both the inflection and the negative slope on the Arrott plots can be observed in Figure 4, which once again proves that obvious first-order magnetic transition occurred. In addition, the inclination degree of the negative slope could largely predict the intensity of the lowest maximal value of $-\Delta S$ (i.e., $-\Delta S_M$) [21].
The negative slope of the LaFe$_{11.5}$Si$_{1.5}$ magnetization isotherms in Figure 3, the temperature step is 2 K in the vicinity of $T_C$ and 5 K for the range far away from $T_C$.

![Magnetization isotherms of LaFe$_{11.5}$Si$_{1.5}$, La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$, and LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ compounds.](image)

The Arrott plots of the LaFe$_{11.5}$Si$_{1.5}$, La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$, and LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ as a function of temperature for an external magnetic field change of 0–3 T are shown in Figure 5. The $-\Delta S_M$ values are 18.7 J/kg·K for LaFe$_{11.5}$Si$_{1.5}$, 22.8 J/kg·K for La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$, and 16.4 J/kg·K for LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$. These results verify the previous inference of the Arrott plots. The negative slope of the La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$ compound is the largest in Figure 4 and its $-\Delta S_M$ is also the largest. The MCE value in a variable magnetic field can be determined by the $-\Delta S_M$ value. The La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$ compound has the largest $-\Delta S_M$ value, indicating it has the maximum MCE. The main magnetic properties of the LaFe$_{11.5}$Si$_{1.5}$, La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$, and LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ are summarized in Table 1. In the near future, the use of comprehensive utilization of element substitution and element doping is expected to obtain magnetic refrigeration materials with high $T_C$ and $-\Delta S_M$.

| Sample          | $T_C$/K | Thermal Hysteresis/K | $-\Delta S_M$/J/kg·K |
|-----------------|---------|----------------------|----------------------|
| LaFe$_{11.5}$Si$_{1.5}$ | 194     | 2.8                  | 18.7                 |
| La$_{0.8}$Nd$_{0.2}$Fe$_{11.5}$Si$_{1.5}$ | 188     | 4.3                  | 22.8                 |
| LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ | 232     | 1.3                  | 16.4                 |

Thermal hysteresis was obtained under an external magnetic field of 0.01 T and $-\Delta S_M$ was obtained under an external magnetic field change of 0–3 T.
In this work, the magnetic properties and magnetocaloric effect of the LaFe\(_{11.5}\)Si\(_{1.5}\), La\(_{0.8}\)Nd\(_{0.2}\)Fe\(_{11.5}\)Si\(_{1.5}\), and LaFe\(_{11.5}\)Si\(_{1.5}\)C\(_{0.2}\) compounds were studied. All the compounds crystallized in a single phase with a cubic NaZn\(_{13}\)-type structure. The substitution of 20\% Nd for La in LaFe\(_{11.5}\)Si\(_{1.5}\) can cause lattice shrinkage, accompanied by lower \(T_C\) and higher \(-\Delta S_M\). Furthermore, doping with 20\% C in LaFe\(_{11.5}\)Si\(_{1.5}\) can cause lattice expansion, accompanied by higher \(T_C\) and lower \(-\Delta S_M\). The La\(_{0.8}\)Nd\(_{0.2}\)Fe\(_{11.5}\)Si\(_{1.5}\) compound had the most obvious first-order magnetic transition characteristics, including the most obvious IEM phenomenon, while the LaFe\(_{11.5}\)Si\(_{1.5}\)C\(_{0.2}\) compound had a \(T_C\) that was relatively close to the room temperature. The use of comprehensive utilization of element substitution and element doping is expected to obtain magnetic refrigeration materials with high \(T_C\) and \(-\Delta S_M\).

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