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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 $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$ shrank 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

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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 $LaFe_{13-x}Si_x$ ($1.2 \leq x \leq 1.6$) 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 $LaFe_{13-x}Si_x$ 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 $La_{1-z}Pr_z(Fe_{0.88}Si_{0.12})_{13}$ compound. When $z = 0$, $a = 1.468$ nm and $T_C = 195$ K. Meanwhile, when $z = 0.5$, $a = 1.446$ 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 $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ 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 $LaFe_{11.7}Si_{1.3}N_{1.3}$) 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 $LaFe_{11.5}Si_{1.5}$ compound (i.e., to form a $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$ compound). Meanwhile, the aim of the element-doping scheme is to introduce interstitial C with an atomic coefficient ratio of 20% in the $LaFe_{11.5}Si_{1.5}$ compound (i.e., to form the $LaFe_{11.5}Si_{1.5}C_{0.2}$ compound). This provides an experimental and theoretical basis for the application of the $LaFe_{13-x}Si_x$ compound.

2. Experimental Procedure

The samples of nominal compositions of $LaFe_{11.5}Si_{1.5}$, $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$, and $LaFe_{11.5}Si_{1.5}C_{0.2}$ 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 Kα 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 5×10^{-7} emu. The isothermal magnetic entropy change ($-\Delta S$) was obtained according to the Maxwell relation [20]:

$$\Delta S(T, H) = \int_0^H (\partial M/\partial T)_H dH \quad (1)$$

3. Results and Discussion

The XRD patterns 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 1. According to the comparison with the PDF card in Jade software, all these samples were crystallized in a single phase with a cubic $NaZn_{13}$-type structure (the space group is *Fm-3c*). Compared with the $LaFe_{11.5}Si_{1.5}$, the fact that the Nd had a smaller atomic radius than the La may have caused the lattice shrinkage in the $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$ 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 $LaFe_{11.5}Si_{1.5}C_{0.2}$ 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 $LaFe_{11.5}Si_{1.5}$, $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$, and $LaFe_{11.5}Si_{1.5}C_{0.2}$ 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.

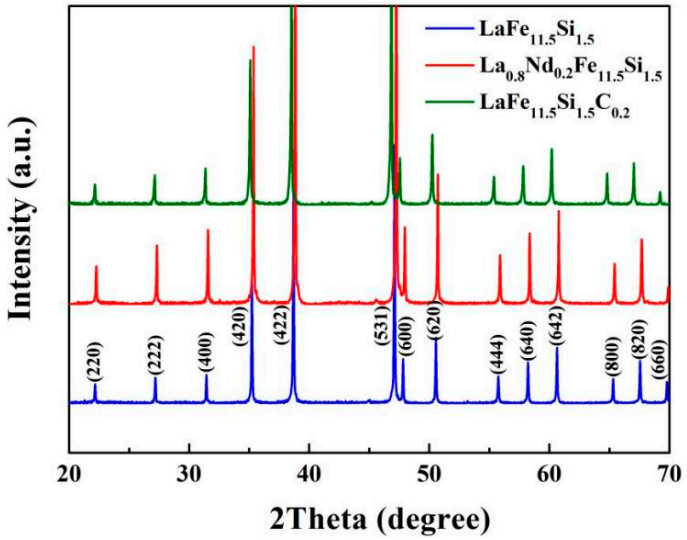


Figure 1. XRD patterns of $LaFe_{11.5}Si_{1.5}$, $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$, and $LaFe_{11.5}Si_{1.5}C_{0.2}$.

The thermomagnetic curves (i.e., *M*-*T* curves) of the $LaFe_{11.5}Si_{1.5}$, $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$, and $LaFe_{11.5}Si_{1.5}C_{0.2}$ under an external magnetic field of 0.01 T are shown in Figure 2. With the increase in temperature, the magnetic transition from the ferromagnetic state to paramagnetic state can be observed in all the samples. The T_C can be defined as the temperature at which the first temperature derivative of the magnetization has its highest value in the heating process [21]. The T_C of the $LaFe_{11.5}Si_{1.5}$, $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$, and $LaFe_{11.5}Si_{1.5}C_{0.2}$ were approximately 194, 188, and 232 K, respectively. The difference in T_C can be explained from the following two perspectives. (1) The change in T_C may have been related to the number of electrons contributed by the different 3*d* elements to the conduction band. The changes in the number of electrons in the conduction band may have led to changes in the 3*d* state density near the Fermi energy [22]. The substitution of La by Nd in the $LaFe_{11.5}Si_{1.5}$ may have reduced the number of 3*d* electrons, resulting in a lower T_C. Correspondingly, the introduction of interstitial C in the $LaFe_{11.5}Si_{1.5}$ may have increased the number of 3*d* electrons, resulting in a higher T_C. (2) The T_C is closely related to the Fe-Fe bond length, especially the $Fe_I(8b)$-$Fe_{II}(96i)$ 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 T_C. 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 T_C. 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 $LaFe_{11.5}Si_{1.5}$, $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$, and $LaFe_{11.5}Si_{1.5}C_{0.2}$ were approximately 2.8, 4.3, and 1.3 K, respectively.

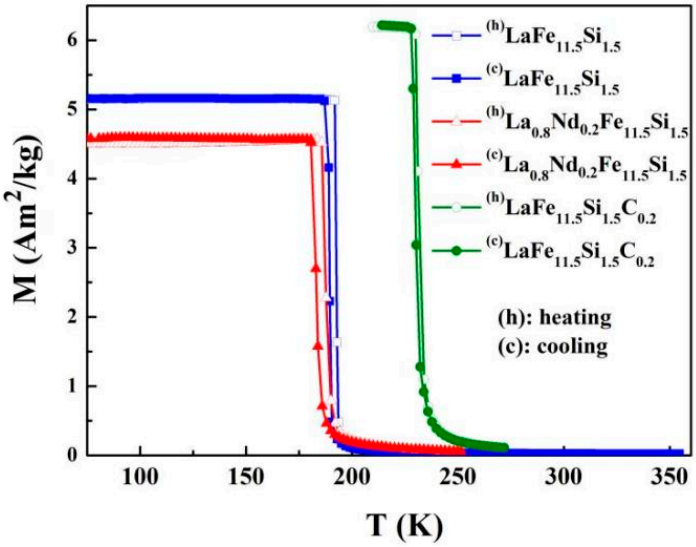


Figure 2. Temperature dependence of magnetization for $LaFe_{11.5}Si_{1.5}$, $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$, and $LaFe_{11.5}Si_{1.5}C_{0.2}$ under an external magnetic field of 0.01 T.

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].

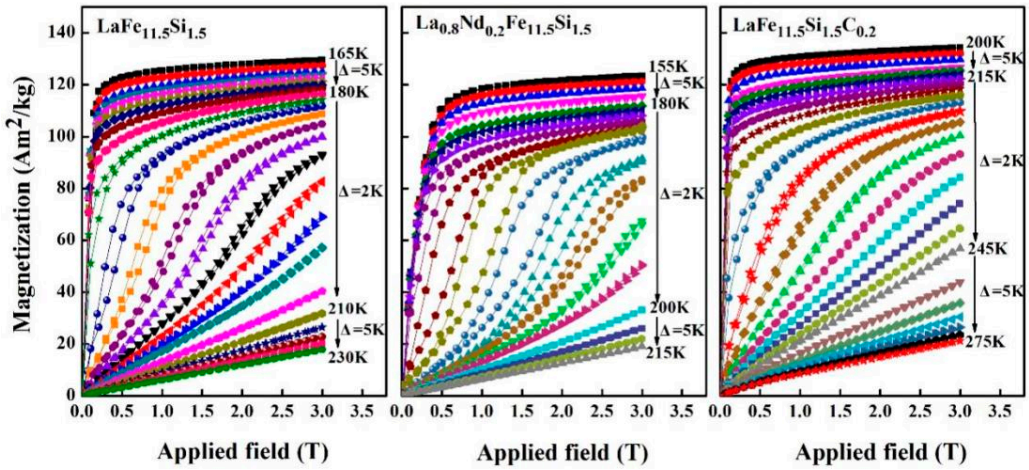


Figure 3. Magnetization isotherms of $LaFe_{11.5}Si_{1.5}$, $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$, and $LaFe_{11.5}Si_{1.5}C_{0.2}$. Temperature steps are 2 K in the vicinity of T_C and 5 K for the range far away from T_C.

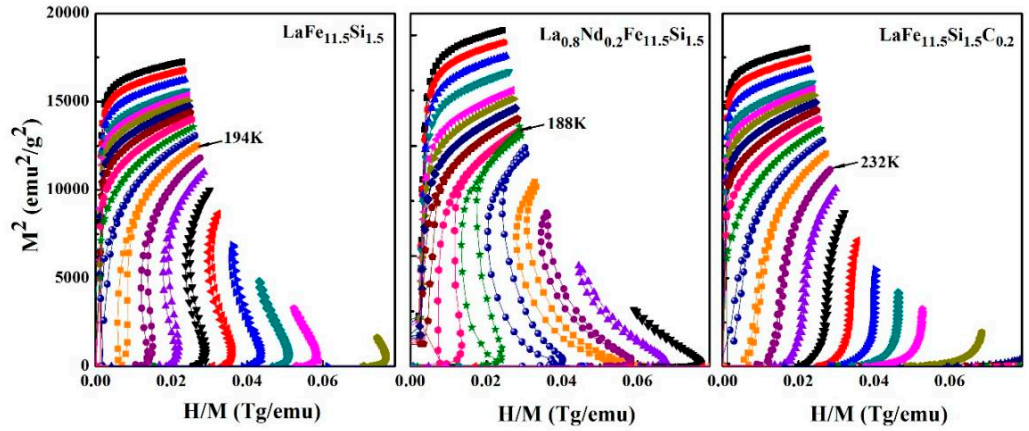


Figure 4. The Arrott plots of $LaFe_{11.5}Si_{1.5}$, $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$, and $LaFe_{11.5}Si_{1.5}C_{0.2}$ compounds.

The $-\Delta S$ 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 $-\Delta S_M$.

Table 1. The main magnetic properties of $LaFe_{11.5}Si_{1.5}$, $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$, and $LaFe_{11.5}Si_{1.5}C_{0.2}$.

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.

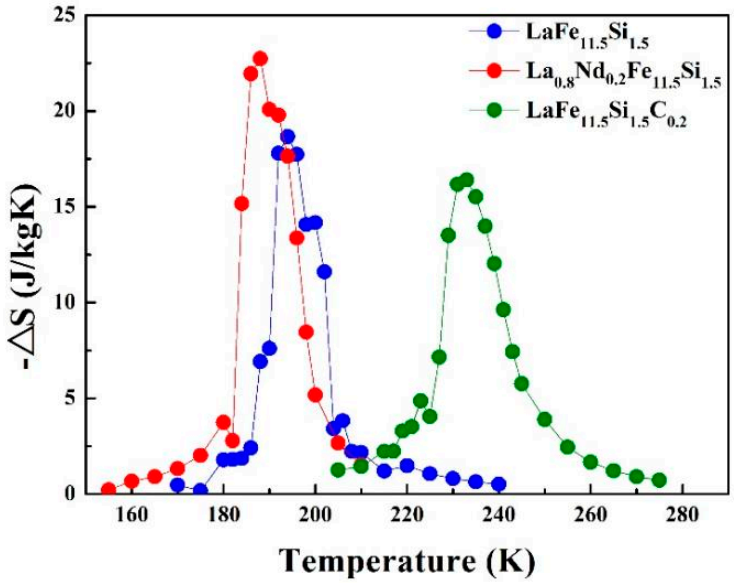


Figure 5. Magnetic entropy change in $LaFe_{11.5}Si_{1.5}$, $La_{0.8}Nd_{0.2}Fe_{11.5}Si_{1.5}$, and $LaFe_{11.5}Si_{1.5}C_{0.2}$ as a function of temperature for an external magnetic field change of 0–3 T.

4. Conclusions

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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