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Influence of particle size on the hydrogenation in La(Fe, Si)$_{13}$ compounds

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The influence of particle size on the hydrogenation of La(Fe, Si)$_{13}$ compounds is studied in detail. The average T_C increases largely from 240 K to 308.5 K due to the enhancement of surface area by reducing the particle size. Besides, it is found that small particle size and narrow size range would improve the homogeneity of hydrogen distribution. The magnetic entropy change (ΔS_M) decreases slightly after hydrogenation, but the maximum value of $-\Delta S_M$ of small $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ still remains a relatively large value of 14.4 J/kg K for a low magnetic field change of 2 T. It is also noted that the hydrogen-saturated $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ exhibits a great stability under a high pressure of 1.36 GPa, and this result is favorable to the further processing and applications of La(Fe, Si)$_{13}$ compounds. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4794975]

Since the discovery of giant magnetocaloric effect (MCE) in $Gd_5(Si_{1-x}Ge_x)_4$,[1] room temperature magnetic refrigeration based on MCE has been demonstrated to be a promising alternative technology to the conventional vapor-compression refrigeration because of its energy saving and environmental friendly. A great deal of efforts has been made to search suitable refrigerants for magnetic refrigeration around room temperature.[2–6] As one of the typical room-temperature magnetic refrigerants, $NaZn_{13}$-type $LaFe_{13-x}Si_x$ compounds with $x \leq 1.6$ exhibit a large magnetic entropy change in the vicinity of Curie temperature T_C, which is due to the first-order magnetic phase transition coupled with field-induced itinerant electron metamagnetic (IEM) transition.[2,7] However, the T_C of $LaFe_{13-x}Si_x$ is usually lower than 210 K, which is not close to room temperature.[8,9] Previous studies have proved that the introduction of interstitial H atoms would result in lattice expansion and enhance T_C largely to about 350 K. Meanwhile, the MCE of hydrides still remains high due to the preservation of first-order phase transition.[10,11] The phase transition temperature is quite sensitive to hydrogen content, and thus it is important to control the process of hydrogenation precisely. There are several factors, i.e., temperature, pressure, time, particle size, etc., which would affect the hydrogen absorption. In comparison with other parameters, particle size control is considered as the easiest and safest way to improve the process of hydrogenation. In addition, it is recently reported that reduction of particle size could help lower the magnetic hysteresis by increasing the surface area of sample and partially removing internal strain and grain boundaries.[12] Consequently, it is necessary to investigate the influence of particle size on the hydrogenation.

It is found that $LaFe_{13-x}Si_xH_y$ compounds show a poor thermal stability, and may dehydrogenate at about 450 K or even decompose into inhomogeneous phases around T_C.[13,14] However, the stability of hydrides under pressure has not yet been reported. Very recently, Lyubina *et al.* reported the good mechanical properties and low magnetic hysteresis of porous La(Fe, Si)$_{13}$ compounds, suggesting that pressing material into porous form may be an effective way to improve the applications of La(Fe, Si)$_{13}$ in refrigerators.[15] Therefore, it is also of importance to study the stability of hydrides under pressure. In present paper, the influence of particle size on the hydrogenation of La(Fe, Si)$_{13}$ compounds as well as the stability of hydrides under high pressure are studied in detail.

The $LaFe_{11.7}Si_{1.3}C_{0.2}$ sample was prepared by arc-melting appropriate proportions of constituent components with the purity better than 99.9 wt. %. The obtained ingot was wrapped in molybdenum foils, sealed in a high-vacuum quartz tube, annealed at 1373 K for a week and then quenched into liquid nitrogen. Powder X-ray diffraction (XRD) measurement was performed at room temperature by using Cu $K\alpha$ radiation and it confirms that the annealed sample crystallizes in a nearly single $NaZn_{13}$-type phase. The bulk $LaFe_{11.7}Si_{1.3}C_{0.2}$ was crushed into small particles (particle size < 1.5 mm) and then annealed in a hydrogen atmosphere of 0.2 MPa at 623 K for 6 h. After hydrogenation, these particles were further divided into three different size ranges using sieves as follows: big size (0.6–1.5 mm), middle size (0.3–0.6 mm), and small size (0–0.3 mm). Magnetizations were measured as functions of temperature and magnetic field by employing a commercial superconducting quantum interference device (SQUID) magnetometer from Quantum Design Inc.

Figures 1(a)–1(c) show the temperature (T) variation of magnetizations (M) under 0.05 T for parent $LaFe_{11.7}Si_{1.3}C_{0.2}$

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compared with $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ with different particle sizes, respectively. Three particles of each size were randomly selected and measured to investigate the homogeneity of the hydrogen absorption. The Curie temperature T_C, defined by the minimum of the dM/dT vs. T curves, is found to be 212 K, 225–255 K, 265–290 K, and 304–313 K for parent $LaFe_{11.7}Si_{1.3}C_{0.2}$ and $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ with different particle sizes, respectively. It is clearly seen that the average T_C increases largely from 240 K (big size) to 308.5 K (small size) with the reduction of particle size. Considering that the average size of different particles is 1.05 mm (big size), 0.45 mm (middle size), and 0.15 mm (small size), respectively, the ratio of surface area to volume is estimated to be 1:2.3:7. Therefore, the enhancement of T_C is due to the fact that the surface area of sample becomes larger so that more hydrogen atoms could enter the crystal structure easily. In addition, it is also noted the temperature span of T_C decreases from 30 K to 9 K with the reduction of particle size and size range. Especially, the temperature span reduces significantly from 25 K of middle size to 9 K of small size by only decreasing the particle size. As is well known, the T_C is sensitive to the content of hydrogen and thus inhomogeneous absorption of hydrogen atoms may lead to the quite different T_C in hydrides.[10,16,17] The present result suggests that small particle size and narrow size range would improve the homogeneity of hydrogen distribution. In comparison with other parameters such as temperature, pressure, and time during hydrogenation, size control of particles may be a much easier and safer way to accelerate the hydrogenation and tune the T_C precisely.

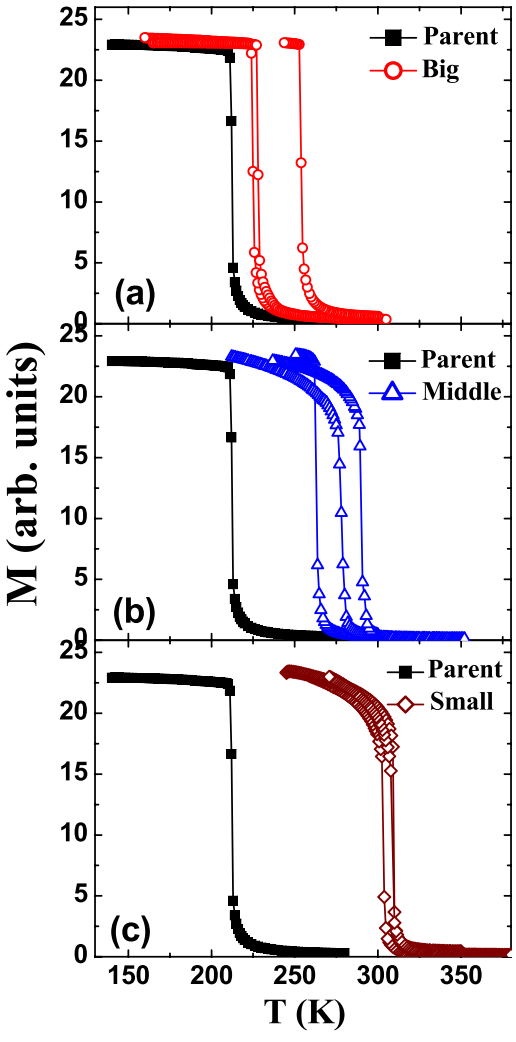

FIG. 1. Temperature dependence of magnetizations under 0.05 T for parent $LaFe_{11.7}Si_{1.3}C_{0.2}$ compared with $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ with different particle sizes, respectively.

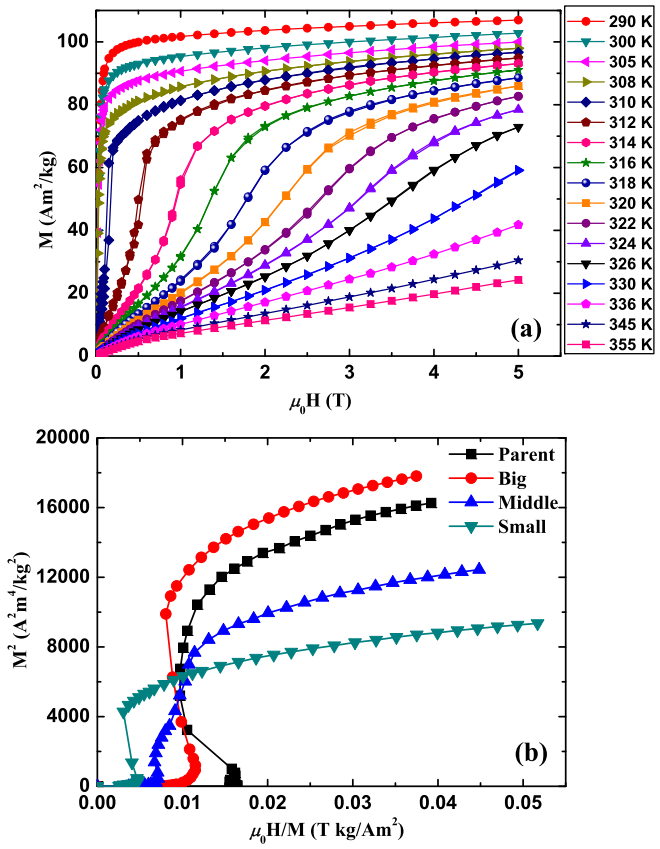

FIG. 2. (a) Magnetization isotherms of small $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ measured around $T_C = 312$ K. (b) Arrott plots for the studied compounds just above their respective T_C.

To compare the MCE of $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ with different particle sizes, one particle of each size, whose T_C is in the middle of the three particles (see Fig. 1), was chosen to be further investigated. Figure 2(a) shows the magnetization isotherms of small $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ measured around $T_C = 312$ K. A sharp change of magnetization is observed above a critical field, indicating the characteristic of first-order field-induced IEM transition above T_C. The maximum value of magnetic hysteresis loss, defined as the enclosed area between the ascending and descending M-H curves, is estimated to be ~2.0 J/kg, which is lower than that of parent compound (5.3 J/kg).[6] Figure 2(b) shows the Arrott plots for $LaFe_{11.7}Si_{1.3}C_{0.2}$, big $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ ($T_C = 229$ K), middle $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ ($T_C = 278$ K), and small $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ ($T_C = 312$ K), just above their respective T_C. The negative slope of Arrott plots confirms the nature of first-order magnetic transition for all the compounds. Besides, it is found that the negative slope declines with reducing the particle size, indicating the weakening of the

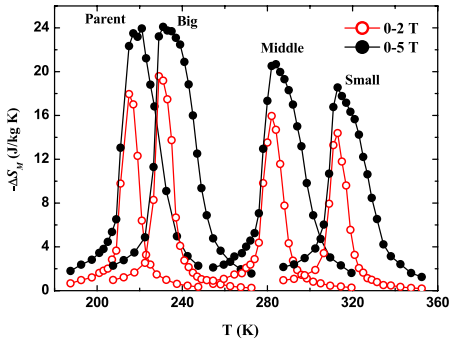

FIG. 3. Temperature dependence of ΔS_M under the magnetic field changes of 2 T and 5 T, respectively.

characteristic of first-order IEM transition with the insertion of H atoms.

The magnetic entropy change (ΔS_M) is calculated from the magnetization isotherms by using Maxwell relation $\Delta S_M = \int_0^H (\partial M/\partial T)_H dH$.[18] Figure 3 displays the ΔS_M as a function of temperature under the field changes of 2 T and 5 T, respectively. It can be seen that all $-\Delta S_M$ peaks broaden asymmetrically toward high temperatures with increasing field, further proving the occurrence of field-induced IEM transition above T_C. The maximum value of $-\Delta S_M$ decreases from 23.9 J/kg K (parent compound) to 18.6 J/kg K (small size) for a field change of 5 T, which is due to the weakening of first-order phase transition by hydrogenation. However, the ΔS_M of small $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$, especially under low magnetic field change of 2 T ($\Delta S_M = 14.4$ J/kg K), still remains higher than those of some magnetocaloric materials around room temperature.

In order to investigate the stability of hydrides under pressure, some small $LaFe_{11.7}Si_{1.3}C_{0.2}$ particles were annealed in the hydrogen atmosphere for a long time until saturation, and then the saturated $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ (x is determined to be 1.7) particles were pressed into a compact plate of $\Phi = \sim 5$ mm by applying a high pressure of 1.36 GPa at room temperature (the inset of Fig. 4). Figure 4 shows the M-T curves measured before and after press under 0.05 T for $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$. It is found that the T_C remains 320 K consistently before and after press. This result indicates the great stability of hydrogenised La(Fe, $Si)_{13}$ compounds under high pressure, which is beneficial to the further processing and practical applications.

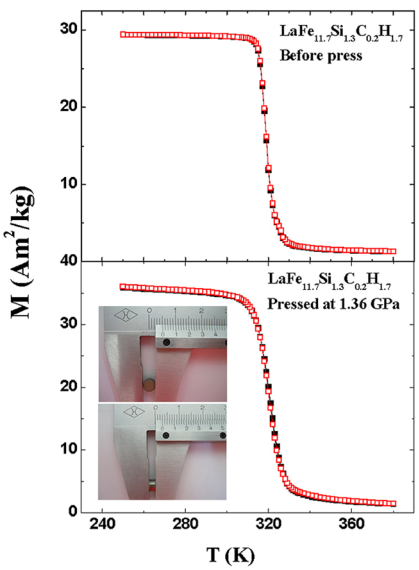

FIG. 4. Temperature dependence of magnetizations measured before and after press under 0.05 T for $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$. The inset shows the images of the compact plate.

In summary, the reduction of particle size leads to a large enhancement of surface area of La(Fe, $Si)_{13}$ compounds, thus accelerating the hydrogenation and tuning the average T_C from 240 K (big size) to 308.5 K (small size) easily. Moreover, the homogeneity of hydrogen distribution is also improved notably by reducing particle size and size range. The hysteresis loss and magnetic entropy change for $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ decrease slightly due to the weakening of first-order IEM transition by hydrogenation. The hydrogen-saturated $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ exhibits an excellent stability under a high pressure of 1.36 GPa. Consequently, particle size control may be a much easier and safer way to improve the hydrogenation effectively and would be helpful to the practical applications of La(Fe, $Si)_{13}$ compounds.

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