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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 ($\Delta S_M$) decreases slightly after hydrogenation, but the maximum value of $-\Delta S_M$ of small LaFe$_{11.7}$Si$_{1.3}$C$_0.2$H$_{1.7}$ 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.

Since the discovery of giant magnetocaloric effect (MCE) in Gd$_x$(Si$_{1-x}$Ge$_x$)$_{13}$, 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. 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. However, the $T_C$ of LaFe$_{13-x}$Si$_x$ is usually lower than 210 K, which is not close to room temperature. Previous studies have proved that the introduction of interstitial H atoms would result in lattice expansion and enhance the 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. However, the $T_C$ of LaFe$_{13-x}$Si$_x$ is usually lower than 210 K, which is not close to room temperature. 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.

It is found that LaFe$_{13-x}$Si$_x$H$_y$ compounds show a poor thermal stability, and may dehydrogenate at about 450 K or even decompose into inhomogeneous phases around $T_C$. 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. Therefore, 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$_0.2$...
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.

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 the studied compounds just above their respective $T_C$. The negative slope of Arrott plots confirms the nature 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 the studied compounds just above their respective $T_C$. The negative slope of Arrott plots confirms the nature 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).$^6$

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

The magnetic entropy change ($\Delta S_M$) is calculated from the magnetization isotherms by using Maxwell relation $\Delta S_M = \int_0^H (\partial M/\partial T)_H dH$. Figure 3 displays the $\Delta S_M$ 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 $\Delta S_M$ of small LaFe$_{11.7}$Si$_{1.3}$C$_{0.2}$H$_x$ decreases 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$_x$ 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.

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 $T_C$ 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.

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