Negative thermal expansion in cubic and tetragonal structure coexisted La(Fe, Si)₁₃ hydride

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Abstract. In this research, the cubic and tetragonal crystal structure coexisted LaFe₁₀₀Si₃₀ compound and its hydride have been prepared by the arc-melting method and the novel electrolytic hydriding. Furthermore, the crystal structure, magnetic and negative thermal expansion (NTE) properties of LaFe₁₀₀Si₃₀ and its hydride were investigated by the X-ray diffraction (XRD) and physical property measurement system (PPMS). Intriguingly, the NTE operation-temperature window of LaFe₁₀₀Si₃₀ has been broadened significantly after introducing interstitial hydrogen atoms. The further magnetic characterizations combined with theoretical analysis reveal that the increase of ferromagnetic to paramagnetic transition temperature due to stronger Fe-Fe magnetic exchange interactions contribute to the broad NTE operation-temperature window in the LaFe₁₀₀Si₃₀ hydride.

1. Introduction
The volume of most materials expand as the temperature rises, while some rare materials have the opposite properties, that is, their volume contract when they are heated. This anomalous volumetric effect is regarded as negative thermal expansion (NTE) properties, which can be utilized by blending the NTE materials with positive thermal expansion (PTE) materials to tailor the thermal expansion coefficient (TEC) of composites. The NTE materials can be applied to many precision instruments due to their ability in controlling thermal expansion, such as in the fiber-optic system, optical mirrors, printed circuit boards and machinery parts. In recent years, several categories of NTE materials have been found, such as ZrW₂O₈ compounds[1,2], ScF₃-based compounds[3-5], PbTiO₃[6,7], LiBeBO₃[8], MnCoGe-based compounds[9], Au nanoparticles[10], antiperovskite manganese nitrides[11-13] and cubic La(Fe, Co, Si)₁₃ compounds[14]. In the above NTE materials, the cubic NaZn₁₃-type La(Fe, Si)₁₃-based compounds are recently developed as promising NTE materials owing to assembling the isotropic NTE and broad NTE operation-temperature window, the excellent electric/thermal conductivity and the outstanding mechanical performance.

The NTE properties of cubic La(Fe, Si)₁₃-based compounds are discovered when the researchers investigate their giant magnetocaloric effect, and they find that the ferromagnetic-paramagnetic (FM–PM) transition and the concurrent lattice contraction occurs around the Curie temperature (T_c) with increasing temperature. Recently, the NTE properties of cubic La(Fe, Si)₁₃ compounds have been

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discussed systematically by partially replacing La or Fe atoms with Co, Pr and Mn atoms[15]. Furthermore, the NTE properties with broad operation-temperature window have been achieved after further substituting Fe with Si, and the reason for that is the structural transition from cubic (Fm3c) structure to tetragonal (I4/mcm) structure[16]. According to previous researches, the NTE properties of La(Fe,Si)13 are induced by the magneto-volume effect (MVE), that is, FM–PM magnetic transition and spontaneous magnetostriction. Furthermore, the magnetic properties of La(Fe,Si)13 are determined by the strength of Fe–Fe magnetic exchange interactions in the cubic NaZn13-type crystal structure. The magnetic exchange interactions are dominated by the interplay between Fe 3d electrons, which is intimately correlated with the Fe–Fe interatomic distance and the crystal structure. According to our previous study, the interstitial atoms would strengthen the Fe–Fe magnetic exchange couplings and further broaden the NTE operation-temperature window of LaFe13−xSi x (1.5≤x≤2.4) compounds with cubic crystal structure. Nevertheless, the effect of interstitial atoms on the NTE properties of cubic and tetragonal crystal structure coexisted LaFe13−xSi x (2.6<x<3.2) compounds have rarely been explored in the past years.

In our study, we investigated the crystal structure, magnetic and thermal expansion properties of LaFe10.0Si13.0 and its interstitial hydride. The experimental results indicate that the LaFe10.0Si13.0 and its hydride include both cubic and tetragonal crystal structure. Furthermore, the NTE operation-temperature window of LaFe10.0Si13.0 have been extended from 160 K (20~180K) to 280K (20~300K) after doping interstitial hydrogen atoms. The FM–PM transition move to high temperature according to thermomagnetic curves, which coincides well with the variations of NTE properties between LaFe10.0Si13.0 and its hydride.

2. Experimental information

The polycrystalline samples with nominal composition LaFe10.0Si13.0 (LFS) were fabricated by the arc-melting method under high-purity argon atmosphere. The raw materials of La, Fe and Si powder are at least 99.9 wt. % in purity. An excess of 10 at % La over the stoichiometric composition was added to compensate for loss during melting. Button samples were melted four times, and each time during melting the buttons were turned over to ensure homogeneity. Then, the arc-melted ingots were sealed in a quartz tube of high vacuum and heat treated at 1050 °C for 20 days in the box furnace, subsequently quenched quickly into ice water. The hydriding process for LFS was performed in a two-electrode electrolytic cell at room temperature (t=6h,12h) and the electrolyte is 3 mol/L NaOH solution. The stainless-steel gauze and Pt operate as cathode and counter electrode. The powder X-ray diffraction measurements were performed by using Cu Ka radiation on a BRUKER D8-discover diffractometer. The lattice parameters were carefully calculated by using JADE and a cubic (Fm3c) model. Magnetizations were measured as a function of temperature by employing physical property measurement system (PPMS-14T, Quantum Design) equipped with AC Magnetometer System(ACMS) option.

3. Results and discussion

3.1. Phase composition and crystal structure

Figure 1 displays the X-ray diffraction patterns of LFS and its hydride at room temperature. The characteristic diffraction peaks shown in the pattern indicate that both LFS and its hydride have a dominating phase adhering to the NaZn13-type structure (space group, Fm3c). However, the diffraction peaks become weaker and broader compared with LaFe13−xSi x compounds with lower Si content, which reveals that tetragonal structure is introduced in the cubic structure matrix with increasing Si content. Therefore, the LFS compound is formed by both cubic and tetragonal crystal structure. Furthermore, all the diffraction peaks shift toward low-angle positions, that is, the lattice expands with increasing hydriding time according to Bragg equation (2dsinθ = nλ). The inset shows the variation of lattice constant with hydriding time, which grows remarkably from 11.417Å to the final 11.456Å. In
theory, the expansion of unit cell with hydriding time demonstrates that the hydrogen atoms insert into the space between La atoms and indeed produce cubic and tetragonal structure coexisted LFS hydride. Furthermore, the lattice parameters of LFS hydride with 12h have not increased with increasing hydriding time indicating the maximum hydrogen capacity in LFS compound. Therefore, the thermal expansion and magnetic properties of LFS hydride with saturated hydrogen concentration have been investigated in this research.

![Figure 1](image1.png)

**Figure 1.** X-ray diffraction patterns for samples of LaFe_{10.0}Si_{3.0} and its hydrides at room temperature. The inset shows the variation of lattice parameter with hydriding time.

### 3.2. Thermal expansion properties

![Figure 2](image2.png)

**Figure 2.** X-ray diffraction patterns for LaFe_{10.0}Si_{3.0} and its hydride from 20 to 260 K.

The variable-temperature X-ray diffraction data was obtained to inspect the crystal structure and the variation of lattice parameter at different temperatures, that is, thermal expansion properties. Figure 2 shows the X-ray diffraction patterns for LFS and its hydride from 20 to 260 K. All the characteristic diffraction peaks belonging to cubic structure matrix retain well, indicating that no crystal structural transition occur in the whole tested temperature range. According to previous reports, the LFS compound possesses NTE properties at cryogenic temperature. Figure 3 displays the position variation of (4 2 2) peak for LFS and its hydride from 20 to 260 K. As is shown in figure 3(a), the (4 2 2) peak of LFS shift to high-angle position from 20 to 180 K revealing that lattice shrinks according to Bragg equation. Nevertheless, positive thermal expansion happens from 180 to 260 K as the diffraction peaks move to low angles. Intriguingly, the (4 2 2) peak of LFS hydride, as displayed in figure 3(b), shifts toward high angles in the tested temperature range from 20 to 260 K, demonstrating...
that the NTE operation-temperature window of LFS extends to room temperature after introducing interstitial hydrogen atoms. Table 1 presents the lattice parameters of LFS and its hydride at different temperatures, the average TECs in the NTE operation-temperature window of which, defined as \( \frac{(\Delta a/a_{300K})_T_2 - (\Delta a/a_{300K})_T_1)}{(T_2-T_1)} \) (\( \Delta a = a-a_{300K} \)), are \(-10.9\times10^{-6} \text{ K}^{-1}\) (20–180 K) and \(-9.5\times10^{-6} \text{ K}^{-1}\) (20–300 K), respectively. Therefore, the NTE operation-temperature window of LFS has been broadened remarkably and its strength of NTE behavior has almost retained after introducing the interstitial hydrogen atoms.

![Figure 3](image1.png)

**Figure 3.** X-ray diffraction spectra of (4 2 2) peak for LaFe\(_{10.0}\)Si\(_{3.0}\) and its hydride from 20 to 260 K.

### Table 1. The lattice parameters of LaFe\(_{10.0}\)Si\(_{3.0}\) and its hydride from 20 to 300 K.

| T/K   | 20  | 60  | 100 | 140 | 180 | 220 | 260 | 300 |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|
| \(a/\text{Å}\) | 11.423 | 11.418 | 11.414 | 11.413 | 11.403 | 11.410 | 11.411 | 11.417 |
| \(a_H/\text{Å}\) | 11.486 | 11.483 | 11.482 | 11.482 | 11.481 | 11.477 | 11.470 | 11.456 |

### 3.3. Magnetic properties

![Figure 4](image2.png)

**Figure 4.** Temperature dependent magnetization between 5 and 300 K in a magnetic field of 0.05T for LaFe\(_{10.0}\)Si\(_{3.0}\) and its hydride. The inset displays the first derivative of magnetization (dM/dT) curves.
As mentioned before, the NTE properties of La(Fe,Si)$_{13}$ compounds are intimately correlated with their magnetic properties. Hence, the thermomagnetic properties of LFS were investigated in order to better comprehend the improvements of NTE properties after hydriding. As is shown in figure 4, the curves of LFS and its hydride decrease gradually around the Curie temperature ($T_c$) indicating that the magnetic transition from ferromagnetic phase to paramagnetic phase occurs. However, the magnetic transition temperature, that is, the Curie temperature ($T_c$) moves to high temperature with doping interstitial hydrogen atoms, which agrees well with the variations of the NTE operation-temperature window. As displayed in the inset of figure 4, the Curie temperature ($T_c$) of LFS and its hydride are determined by the temperature corresponding to the minimum $dM/dT$ value. According to this principle, the $T_c$ values of LFS and its hydride are 175.4 and 230.2K. Therefore, the extension of NTE operation-temperature window of LFS after hydriding is attributed to the increase of magnetic transition temperature, that is, the Curie temperature ($T_c$).

Generally speaking, the magnetic transition temperature ($T_c$) reflects the strength of magnetic exchange couplings in the La(Fe,Si)$_{13}$ compounds. Furthermore, it is well known that the exchange interactions of rare-earth (R=La) transition-metal (T=Fe) compounds are determined by the T-T, R-T and R-R interactions, and the T-T interaction is the strongest among them. Therefore, the $T_c$ is mainly affected by the Fe-Fe interactions. In LFS compound, the interatomic distance of Fe-Fe atoms would increase owing to introducing interstitial hydrogen atoms between La atoms, which can enhance the Fe-Fe exchange interactions by reducing the overlap of the Fe 3d wave functions. Therefore, the Curie temperature ($T_c$) and coupling NTE operation-temperature window would shift to high temperature in the LFS hydride.

4. Conclusions

In summary, the effect of interstitial hydrogen atoms on the NTE operation-temperature window and thermal expansion coefficient of LFS have been systematically investigated in our research. The experimental results indicate that the NTE operation-temperature window of LFS have been broadened from 160K (20–180K) to 280K (20–300K) after introducing interstitial hydrogen atoms. More fascinatingly, the strength of NTE behavior almost retain in the LFS hydride. Therefore, the LFS hydride with broader NTE operation-temperature window and relatively strong NTE properties can be potentially applied in the precision instruments operating from cryogenic temperature to ambient temperature.

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