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Cryogenic abnormal thermal expansion property of carbon-doped La(Fe,Si)₁₃ compounds

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Recently, the La(Fe,Si)₁₃-based compounds have attracted much attention for their isotropic and tunable abnormal thermal expansion (ATE) property as well as bright prospect of practical applications. In this research, we have prepared the cubic NaZn₁₃type carbon-doped La(Fe,Si)₁₃ compounds by the arc-melting method, the ATE and magnetic property of which were investigated by means of variable-temperature X-ray diffraction, strain gauge and physical property measurement system (PPMS). The experimental results indicate that both micro and macro linear thermal expansion behavior gradually weaken with the increase of interstitial carbon atoms. Moreover, the temperature region with the most remarkable negative thermal expansion (NTE) property have been broadened and near zero thermal expansion (NZTE) behavior occurs in the bulk carbon-doped La(Fe,Si)₁₃ compounds.

Introduction

Abnormal thermal expansion (ATE) materials have captured much attention in recent years due to the urgent demand in the high-tech fields. Much stricter precision criteria requires a precisely tailored thermal expansion or even zero thermal expansion in many devices along with the scientific and technological evolution. For example, the potential applications in the optical mirrors, fibre-optic system, printed circuit boards, and machinery parts. Abnormal thermal expansion materials include near zero thermal expansion (NZTE) materials and negative thermal expansion (NTE) materials, respectively. The NTE materials exhibit abnormal volumetric effect that their volume contract rather than expand when they are heated, which can be blended with the positive thermal expansion (PTE) materials to form composites with accurate thermal expansion coefficient (TEC). In the past decades, several categories of NTE materials have been discovered, such as the materials family of ZrW₂O₈,^{1,2} ScF₃-based compounds,³⁻⁵ CuO nanoparticles,⁶ compounds,⁷⁻⁹ PbTiO₃-based antiperovskite manganese nitrides, 10-13 LiBeBO₃,¹⁴ Y₂Mo₃O₁₂,^{15,16} MnCoGe-based compounds¹⁷ and La(Fe,Co,Si)₁₃ compounds.¹⁸ However, the actual applications of some NTE materials have been restricted due to the relatively narrow temperature window, limited NTE coefficient, thermal expansion anisotropy, low mechanical strength and low thermal conducting property. Recently, the La(Fe,Si)₁₃-based compounds have been developed as promising NTE materials owing to assembling the isotropic NTE, the excellent electric/thermal conductivity and the outstanding mechanical performance.

The cubic NaZn₁₃-type La(Fe,Si)₁₃-based compounds have been well-known for their potential applications in magnetic refrigeration fields due to giant magnetocaloric effect. Previous literatures have demonstrated that the magnetocaloric effect originates from the ferromagnetic (FM) to paramagnetic (PM) transition and the concurrent lattice contraction around the Curie temperature (T_c) with the increase of temperature. Fascinatingly, the practical application prospect of La(Fe,Si)₁₃ as NTE materials has recently been discussed by means of partial substitution of Co for Si.¹⁸ In the La(Fe,Si)₁₃ compounds, positive thermal expansion is induced by anharmonicity of lattice, whereas NTE behavior is attributed to spontaneous magnetostriction effect below T_c and magnetic phase transition, i.e., magneto-volume effect (MVE).¹⁹ When MVE effect counteracts or even exceeds anharmonicity effect of lattice, the ATE behavior appears. Therefore, broader NTE operationtemperature window and enhanced NTE property can be achieved by adjusting magnetic property. The magnetic property of La(Fe,Si)13 is mainly determined by the strength of Fe–Fe magnetic exchange interactions due to the nonmagnetic of La and Si. The magnetic exchange interactions are the consequence of the interplay between 3d electrons of Fe atoms, which is closely correlated with the Fe–Fe interatomic distance and the crystal structure. A variety of excellent NTE materials with the formula La(Fe,M)13 (M=Si,Al) have been reported

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through partial substitution for La or Fe atoms, which will adjust the magnetic property and further improve the coupling NTE property. $^{\rm 20-22}$

In recent years, the researchers have prepared La(Fe,Si)₁₃C_x compounds by adding appropriate amount of Fe-C alloy into the raw materials and investigated their magnetocaloric effect. However, the influence of interstitial atoms such as carbon and hydrogen on the ATE property of La(Fe,Si)₁₃ have rarely been explored in the past years. Here we report the low-temperature ATE behavior of LaFe_{11.5}Si_{1.5}C_x (x = 0, 0.2, 0.4 and 0.6) compounds from both the micro and macro perspective. The experimental results indicate that the NTE operation-temperature window has been broadened with further carbon atom insertion. More interestingly, the bulk LaFe_{11.5}Si_{1.5}C_x (x = 0.2, 0.4 and 0.6) samples show near zero thermal expansion (NZTE) property from 80 to 150 K (~70K), which is much valuable for practical applications in the cryogenic engineering fields.

Experimental procedure

The polycrystalline samples with the nominal composition $LaFe_{11.5}Si_{1.5}C_x$ (x = 0, 0.2, 0.4 and 0.6) were synthesized by arcmelting an appropriate proportion of constituent component under high-purity argon atmosphere. The starting materials of La wire, Fe, Si and SiC powder are at least 99.9 wt. % in purity. Not like the previous study, the content of interstitial carbon atoms are controlled by introducing proper amount of SiC powder in this paper. Besides, an excess 10 at % of La over the stoichiometric composition was added to compensate for loss during melting. The mixture of raw materials were pressed into pellets and then melted four times, and the mass loss after arc melting was less than 1 wt. %. The heat treatment was carried out in a quartz tube of high vacuum at 1050 °C for 20 days in the box furnace, and subsequently quenched quickly into ice water.

The room-temperature and variable-temperature powder X-ray diffraction measurements were performed by using Cu K α radiation on a BRUKER D8-discover diffractometer. The lattice parameters at different temperatures were carefully calculated by using JADE and a cubic (Fm3c) model. The linear thermal expansion data (Δ L/L_{300K}) (Δ L/L= Δ V/3V) were acquired by using a strain gauge over a temperature range of 80-300 K. Magnetizations as a function of temperature were measured by employing physical property measurement system (PPMS-14T, Quantum Design) equipped with AC Magnetometer System (ACMS) option.

Results and discussion

Phase purity and crystal structure

The room-temperature X-ray diffraction data was obtained to inspect the effect of carbon doping on the crystal structure of LaFe_{11.5}Si_{1.5} sample. As is shown in Fig. 1, all the samples have a dominating phase adhering to the NaZn₁₃-type structure (space group, Fm3c) with introducing interstitial carbon atoms. However, a small amount of α -Fe and LaFeSi phase were



Fig.1 X-ray diffraction spectra for samples of $LaFe_{11.5}Si_{1.5}C_x$ (x = 0, 0.2, 0.4 and 0.6) under ambient condition.

detected in the samples, the diffraction peaks of which are marked in the patterns. Particularly, the amount of α -Fe phase in LaFe_{11.5}Si_{1.5}C_{0.6} is relatively high compared with other samples, indicating that the carbon content more than x=0.6 is unfavorable for the formation of cubic NaZn₁₃-type structure. The α -Fe phase of LaFe_{11.5}Si_{1.5}C_{0.6} is calculated about 11.2 wt. % via the Rietveld refinement on the General Structure Analysis System (GSAS) program. Furthermore, we found that all the diffraction peaks for NaZn13-type structure shift toward lowangle positions, that is, the lattice expands with the introduction of carbon atoms. The inset shows the lattice constant of each sample at room temperature refined by the Rietveld method as well, which grows with the increase of nominal carbon content. Theoretically, the expansion of unit cell with nominal carbon content demonstrate that the carbon atoms indeed insert into the space between La atoms and to produce LaFe_{11.5}Si_{1.5}C_x compounds successfully.

Thermal expansion property

The variable-temperature X-ray diffraction measurements were carried out in order to investigate the crystal structure of $LaFe_{11.5}Si_{1.5}C_x$ (x = 0, 0.2, 0.4 and 0.6) and describe their linear thermal expansion property microscopically. As we can see from Fig. S1 to Fig. S4, all the diffraction peaks belonging to the cubic NaZn₁₃-type structure have been remained perfectly, indicating that no crystal structure transition occurs in the whole tested temperature range. Furthermore, the variation of lattice parameters with temperature were acquired and converted to $\Delta a/a_{300K}$ ($\Delta a=a-a_{300K}$) values shown in Fig. 2(a). From this figure, the values of $\Delta a/a_{300K}$ for all samples increase with decreasing temperature in the entire tested temperature range from 70 to 300 K, revealing that negative thermal expansion behavior occurs. Additionally, it is noteworthy that the NTE property is strongly affected by the interstitial carbon atoms. The NTE behavior for samples gradually become weaker with introducing more interstitial carbon atoms. Specifically, the average TECs, defined as $((\Delta a/a_{300K})_{T2}-(\Delta a/a_{300K})_{T1})/(T_2-T_1)$, are - 87.9×10⁻⁶ K⁻¹ and -49.7×10⁻⁶ K⁻¹ between 180 and 250 K for $LaFe_{11.5}Si_{1.5}$ and $LaFe_{11.5}Si_{1.5}C_{0.6}$, respectively. Furthermore, the temperature range with the most remarkable NTE behavior



Fig.2 (a) Temperature evolution of linear thermal expansion $\Delta a/a$ (reference temperature: 300 K) from 70 to 300 K for LaFe_{11.5}Si_{1.5}C_x (x = 0, 0.2, 0.4 and 0.6). (b) Temperature dependence of linear thermal expansion $\Delta L/L$ (reference temperature: 300 K) from 80 to 300 K for LaFe_{11.5}Si_{1.5}C_x (x = 0.2, 0.4 and 0.6).

have been broadened and move to higher temperature region as the amount of carbon content increase from x=0 to x=0.6. For instance, the temperature window with pronounced NTE effect for LaFe_{11.5}Si_{1.5} is about 40 K (180-220 K), while the temperature range for LaFe_{11.5}Si_{1.5}C_{0.6} is as large as 70 K (180-250 K), which is about 70% larger than that of LaFe_{11.5}Si_{1.5}. Intriguingly, the broadened remarkable NTE operation-temperature window achieved by adjusting interstitial carbon content can promote potential applications in the cryogenic engineering.

In the cryogenic fields, the NTE materials are usually used in bulk or mixed with other positive thermal expansion materials to form composite. Therefore, the investigation of macroscopic linear thermal expansion property is essential upon considering the aspect of actual applications. Fig. 2(b) displays the $\Delta L/L_{300K}$ versus T curve from 80 to 300 K for samples of LaFe_{11.5}Si_{1.5}C_x (x=0.2, 0.4 and 0.6). Analogous to the variation of microscopic lattice, all curves increased sharply upon cooling in a certain temperature range, indicating that the series materials of LaFe_{11.5}Si_{1.5}C_x possess the abnormal NTE property in the macroscopic level as well. Additionally, the NTE operationtemperature window also becomes broader and shift toward room temperature as the increase of carbon content. Nevertheless, the variation discrepancy between the microscopic and macroscopic volume will be noted when we give further observations. For example, the macroscopic volume change from 80 to 150 K is closer to near zero thermal expansion (NZTE) than that of the micro level. Moreover, the absolute values of thermal expansion coefficient deduced from $\Delta L/L_{300K}$ are smaller than that from $\Delta a/a_{300K}$. For example, the macro and micro TEC values from 180 to 250 K (ΔT =70 K) for LaFe_{11.5}Si_{1.5}C_{0.6} is -26.3×10⁻⁶ K⁻¹ and -49.7×10⁻⁶ K⁻¹, respectively. It is well known that there exists abundant crystal grains and grain boundaries in the polycrystalline samples. The interstice located between the grain boundaries presents positive thermal expansion behavior, which can weaken the NTE property of the polycrystalline samples and thus contributed to the difference between the micro and macro NTE behavior. Through the above analysis, the similar NTE behavior is observed in the bulk LaFe_{11.5}Si_{1.5}C_x materials, which is beneficial for the practical applications of NTE materials in the cryogenic fields.

Magnetic property

Combined with previous experimental results and theory, the ATE property of La(Fe,Si)₁₃-based compounds is ascribed to magneto-volume effect. Therefore, the temperature dependent magnetizations for LaFe_{11.5}Si_{1.5}C_x (x=0, 0.2, 0.4 and 0.6) were measured under 0.05T in heating process in order to reveal the mechanism behind this abnormal volumetric behavior. As displayed in Fig. 3, the values of magnetization for all samples decreased sharply around Curie temperature (T_c) upon heating, indicating that FM to PM magnetic transition occurs. However, it is noted that the magnetization for LaFe_{11.5}Si_{1.5}C_{0.6} above T_c is much higher than other three samples, which is attributed to the incorporation of α -Fe phase. Furthermore, the Curie temperature is obtained by determining the temperature with the smallest dM/dT value. Based on this



Fig.3 The magnetization under a magnetic field of 0.05T for samples of $LaFe_{11.5}Si_{1.5}C_x$ (x = 0, 0.2, 0.4 and 0.6) as a function of temperature.

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can make the FM to PM cess, as shown in Fig. 3, operation-temperature paper. 1.5C_x (x = 0, 0.2, 0.4 and fully prepared by arc-

principle, the T_c of LaFe_{11.5}Si_{1.5}C_x (x = 0, 0.2, 0.4 and 0.6) is 196.9 K, 242.4 K, 244.4 K and 265.3 K, respectively. Apparently, the T_c move to higher temperature with more carbon atoms inserted into lattice, which can lead to the most pronounced NTE behavior in higher temperature region due to the strong coupling between magnetic transition and NTE property. This relation can be reconfirmed by the similar trend in the micro and macro NTE behavior. Besides, the LaFe_{11.5}Si_{1.5}C_x samples exhibit low thermal expansion coefficient for both the micro the macro thermal expansion below T_c, the reason for which is that ferromagnetic state can suppress the anharmonic lattice vibrations due to spontaneous magnetostriction effect.

Theoretical speculation

The variations of crystal structure for carbon doped LaFe_{11.5}Si_{1.5} compound were analysed due to the close correlations between structure and property. As depicted for cubic NaZn₁₃-type structure in Fig. 4, Fe atoms occupy two nonequivalent sites, i.e., 8b (Fe^I) and 96i (Fe^{II}), respectively. The Fe^I atom is surrounded by an icosahedron with 12 Fe^{II} atoms, and the Fe^{II} atom has 1 Fe¹ atom and 9 Fe¹¹ atoms as the nearest neighbors.²³ According to theory and previous experiment, the Si atoms mostly tend to occupy the Fe^{II} sites to stabilize the crystal structure, and the carbon atoms will insert into the space between La atoms due to their small atomic radius. There exist two types of Fe-Fe magnetic exchange interactions including Fe¹–Fe^{II} and Fe^{II}–Fe^{II} in the La(Fe,Si)₁₃ compounds. However, the energy of magnetic exchange interactions for Fe^I-Fe^{II} is stronger than that for Fe^{II}-Fe^{II} due to shorter Fe^I-Fe^{II} interatomic distance. The magnetic property of LaFe_{11.5}Si_{1.5} is mostly determined by the Fe^I–Fe^{II} magnetic exchange interactions, the variation of which will strongly affect the magnetic transition and the coupling NTE property. Importantly, the interstitial carbon atoms would expand the unit cell and elongate the Fe^I-Fe^{II} interatomic distance concurrently, which can strengthen the Fe-Fe magnetic exchange couplings by reducing the overlap of the Fe 3d wave functions.²⁴ Therefore, materials need absorb more thermal energy to trigger the FM to PM transition with doping carbon atoms. Consequently, the Curie temperature for $LaFe_{11.5}Si_{1.5}C_x$ tend to increase due to the stronger Fe-Fe magnetic exchange couplings. Surprisingly, we find that the NTE behavior weakens with the enhancement of magnetic exchange interactions. According to the results of magnetocaloric effect, the reason for that is the type of magnetic transition transforms



Fig.4 The 12 interstitial sites of cubic NaZn₁₃-type structure (space group Fm3c) for LaFe_{11.5}Si_{1.5} compound that the carbon atoms can occupy. (Note: the 12 crystal sites are partially occupied due to inadequate doped carbon atoms in our study)

from first order to second order, which can make the FM to PM magnetic transition a more gradual process, as shown in Fig. 3, and broaden the remarkable NTE operation-temperature window as previously presented in this paper.

Conclusions

In summary, the NaZn₁₃-type LaFe_{11.5}Si_{1.5}C_x (x = 0, 0.2, 0.4 and 0.6) compounds have been successfully prepared by arcmelting method. The room-temperature powder X-ray diffraction result indicates that carbon content more than x=0.6 is unfavorable for the formation of NaZn₁₃-type crystal structure due to the incorporation of α -Fe phase. Besides, the bulk $LaFe_{11.5}Si_{1.5}C_x$ (x = 0.2, 0.4 and 0.6) compounds display low thermal expansion property from 80 to 150 K (~70 K), which is the result of interplay between spontaneous magnetostriction effect and anharmonic effect of lattice as well as the existence of massive interstice located between grain boundaries. Furthermore, the temperature region where the most remarkable NTE behavior occurs has been broadened due to the transformation of magnetic transition from first order to second order. Consequently, the LaFe11.5Si1.5Cx materials (x=0, 0.2, 0.4 and 0.6) with tunable abnormal thermal expansion property can be potentially applied in the cryogenic engineering fields.

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