Low-temperature abnormal thermal expansion property of carbon-doped La(Fe,Si)$_{13}$ compounds

Shaopeng Li[1,2], Rongjin Huang[1,], Yuqiang Zhao[1,2], Wei Wang[1], Laifeng Li[1,*]*

[1] *State Key Laboratory of Technologies in Space Cryogenic Propellants, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, P.R. China*

[2] *University of Chinese Academy of Sciences, Beijing, P.R. China*

M2PoD-02 [M9]

Background

- 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).
- 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. In the La(Fe,Si)$_{13}$ compounds, positive thermal expansion is induced by anharmonicity of lattice, whereas NTE behavior is attributed to magnetostriction effect, i.e., magneto-volume effect (MVE). When MVE effect counteracts or exceeds anharmonicity effect of lattice, the ATE behavior appears.
- Therefore, broader NTE operation-temperature window and enhanced NTE behavior can be achieved by adjusting magnetic property. Here we prepared LaFe$_{11.5}$Si$_{1.5}$C$_x$ (x = 0, 0.2, 0.4 and 0.6) compounds to explore the effect of interstitial carbon atoms on both the micro and macro low-temperature NTE behavior.

Materials and Methods

Materials Preparation

Polycrystalline samples: LaFe$_{11.5}$Si$_{1.5}$C$_x$ (x = 0, 0.2, 0.4 and 0.6).

Raw materials: La wire, Fe, Si and SiC powder (at least 99.9 wt. % in purity).

Note: 1. The mass for one sample is about 10g.

2. The mass loss for sample after arc melting is less than 1 wt. %.

Raw materials → (Mixed in Ar; Pressed using machine) → Sample pellets → (arc melting in furnace; Ar atmosphere) → Sample ingot → (Annealed 20 days (vacuum); quenched in ice water) → Sample

Measurement Methods

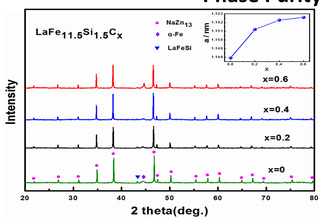
- Powder X-ray diffraction measurements: The BRUKER D8-discover diffractometer (Cu Kα radiation).
- The macro Thermal expansion property: The strain gage with a reference material (ZERODUR glass ceramic).
- Magnetic property: The physical property measurement system (PPMS-14T，Quantum Design) equipped with AC Magnetometer System(ACMS) option.

The right picture shows the arc-melting furnace, which is filled with Ar during melting the sample pellets. The highest temperature is about 3000 ℃ in the furnace.

The right shown is the PPMS, which can be used to measure the magnetization versus temperature and magnetic field curves for samples. The maximum magnetic fields can reach 14T, and the lowest temperature is about 5K.

Results and Discussion Ⅰ

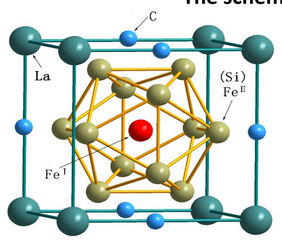
Phase Purity and Crystal Structure



- All the samples have a dominating phase adhering to the NaZn$_{13}$-type structure.
- The carbon content more than x=0.6 is unfavorable for the formation of cubic NaZn$_{13}$-type structure.
- The increase of lattice constant prove that LaFe$_{11.5}$Si$_{1.5}$C$_x$ samples are indeed prepared.

Figure 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.

The schematic of Crystal Structure



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 Fe^{I} atom and 9 Fe^{II} atoms as the nearest neighbors

Figure 2. The NaZn$_{13}$-type structure (space group Fm3c) for samples of LaFe$_{11.5}$Si$_{1.5}$C$_x$.

Results and Discussion Ⅱ

Thermal Expansion Property

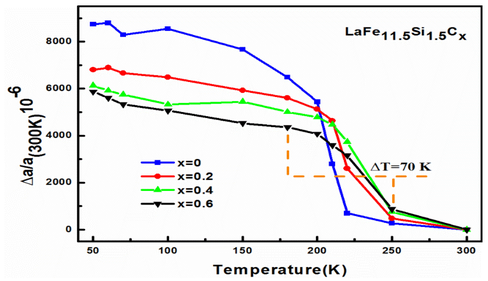


Figure 3. Temperature evolution of linear thermal expansion Δa/a (reference temperature: 300 K) from 50 to 300 K for LaFe$_{11.5}$Si$_{1.5}$C$_x$. (Micro)

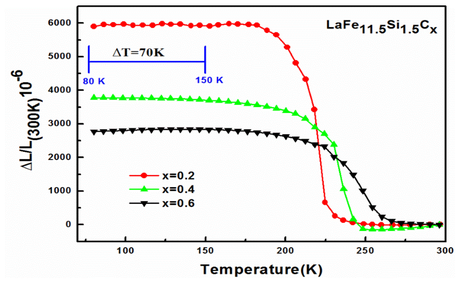
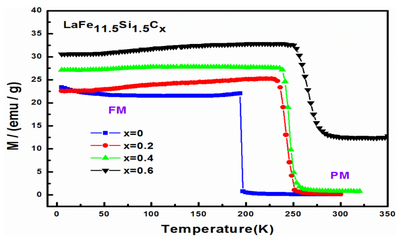


Figure 4. Temperature dependence of linear thermal expansion ΔL/L (reference temperature: 300 K) from 80 to 300 K for LaFe$_{11.5}$Si$_{1.5}$C$_x$. (Macro)

- The micro and macro NTE behavior occurs in the similar temperature region for LaFe$_{11.5}$Si$_{1.5}$C$_x$.
- The macro NTE behavior weakens compared with the variation of micro lattice for LaFe$_{11.5}$Si$_{1.5}$C$_x$.
- The macro thermal expansion from 80 to 150 K is closer to NZTE behavior than that of micro thermal expansion behavior.
- The temperature region with the most remarkable NTE behavior becomes broader with more interstitial carbon atoms.

Magnetic Property



- The values of magnetization for all samples increased sharply around Curie temperature (T_c) upon cooling, indicating that ferromagnetic–paramagnetic transition occurs.
- The T_c move to higher temperature with more carbon atoms inserted into lattice, leading to the most pronounced NTE behavior in higher temperature region.
- The type of magnetic transition transforms from first order to second order, broadening the NTE operation-temperature window.

Figure 5. The magnetization under a magnetic field of 0.05T for LaFe$_{11.5}$Si$_{1.5}$C$_x$ (x = 0, 0.2, 0.4 and 0.6) as a function of temperature.

Conclusion

- The NaZn$_{13}$-type LaFe$_{11.5}$Si$_{1.5}$C$_x$ (x = 0, 0.2, 0.4 and 0.6) compounds have been synthesized by arc-melting method successfully.
- The carbon content in LaFe$_{11.5}$Si$_{1.5}$C$_x$ more than x=0.6 is unfavorable for the formation of NaZn$_{13}$-type phase due to high-content α-Fe.
- 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 interplay between spontaneous magnetostriction and inharmonic lattice vibration.
- The temperature region where the most remarkable NTE behavior occurs becomes broader due to the transformation of magnetic transition from first order to second order.
- The LaFe$_{11.5}$Si$_{1.5}$C$_x$ materials (x=0, 0.2, 0.4 and 0.6) with tunable abnormal thermal expansion property can be potentially applied in the cryogenic fields.

*Corresponding authors: huangrongjin@mail.ipc.ac.cn; laifengli@mail.ipc.ac.cn;