Low-temperature abnormal thermal expansion property of Mn doped cubic NaZn$_{13}$-type La(Fe, Al)$_{13}$ compounds

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Abstract. Low-temperature abnormal thermal expansion (ATE) materials have been recently developed because of their significant applications for cryogenic engineering. However, the challenge still remains for the control of ATE effect at cryogenic temperature and adjustable ATE is of fundamental interest. In this paper, we report the isotropic ATE in La(Fe, Al)$_{13}$ compounds over a wide adjusting temperature range by partially substituting Fe by Mn. It is found that all samples crystallize in the cubic NaZn$_{13}$-type structure with the $Fm\overline{3}c$ space group. The introduction of nonmagnetic Mn atoms reduces the Fe-Fe exchange interaction, therefore, the itinerant electron system needs less energy to break the magnetic order in ferromagnetic (FM) state at low temperature. The negative thermal expansion (NTE) operation-temperature window moves towards lower temperatures accompanied with the decrease of Curie temperature ($T_C$) by increasing Mn elements. Moreover, the composite combining Mn 0 and Mn 57 broadens the zero thermal expansion (ZTE) behavior occurring in the whole tested temperature range. The present studies could be useful to control the thermal expansion, and indicate the potential applications of ATE materials in cryogenic engineering.

1. Introduction

Most materials expand when heated and contract on cooling due to the effect of the anharmonic lattice vibration. The thermal induced strain usually gives rise to materials’ physics and function failure originated from the undesirable mismatch of the coefficient of thermal expansion (CTE) in different components$^{[1]}$ and the decline in the precision of thermometric instruments$^{[2]}$. Therefore the abnormal thermal expansion (ATE) property including zero thermal expansion (ZTE) and negative thermal expansion (NTE) has become an advanced research focus especially in high-precision devices. In recent years, several kinds of materials with ATE property have been discovered, such as LiAlSiO$_4$ ($\beta$-eucryptite), ZrW$_2$O$_8$, ScF$_3$$^{[3]}$, PbTiO$_3$-based compounds$^{[4, 5]}$ La(Fe, Si)$_{13}$-based compounds$^{[7-10]}$ and some antiperovskite manganese nitrides$^{[2, 11]}$. It is noteworthy that most of ATE materials are tuned to adjust the temperature range of ATE moving towards higher temperature span. However, the low-temperature volume control across a wide temperature range is also one of the most important functions and has high potential applications in the rapid developing cryogenic engineering, such as low-
temperature switch, cryogenic valve, piston/piston sleeve of refrigerator and carrying structure of superconducting magnet.[12]

La(Fe, M)$_{12}$-based (M = Si, Al) rare earth intermetallic compounds recently have attracted more considerable attention as the candidates for ATE materials due to their isotropic and controllable ATE properties, simple preparation technology, high electrical and thermal conductivity, and good mechanical performance.[7] The NTE property at low temperature is required to counteract the normal positive thermal expansion (PTE). However, the starting NTE operation-temperature window in ferromagnetic (FM) La(Fe, M)$_{13}$-based compounds is generally above 100 K, which is too high for practical applications in cryogenic engineering.[7, 9] Moreover, nearly ZTE behavior could be observed in some of the materials while most of them show relatively narrow ZTE temperature ranges.[13, 14] Nevertheless, it has been reported that the LaFe$_{11.4}$Al$_{1.6}$ compound shows a slight NTE property in a temperature range 150 - 255 K, and exhibits the ZTE behavior in temperature ranges of 5 - 150 K and 255 - 300 K.[15] Here, we report an effective way to control the ATE behavior shifting towards the lower temperature region and occurring over a large scale by optimizing the chemical composition. We denote the LaFe$_{11.4}$Al$_{1.6}$ compound without Mn dopant as Mn 0. According to the structure analysis, the Mn atoms enter the 96i site substituting for Fe$^0$ randomly, and the Mn occupancy at the site is calculated to be 3.8%, 5.7% and 7.6% for the three prepared samples. Correspondingly, the compounds with the increase of Mn content are denoted as Mn 38, Mn 57 and Mn 76, respectively.

In this letter, the effect of Mn doping on the structural, magnetic and abnormal thermal expansion properties of the LaFe$_{11.4}$Al$_{1.6}$ compound were extensively explored and discussed. All samples have the same cubic NaZn$_{13}$-type structure (space group: $Fm\bar{3}c$). It was found that the NTE temperature window shifts towards the lower temperature region with the increase of Mn concentration. Furthermore, the NTE material Mn 57 can combine the Mn 0 to exhibit ZTE behavior in the temperature range of 150 - 255 K, thus the ZTE operation-temperature window can be broadened to the whole tested temperature range.

2. Experimental procedure

We prepared the polycrystalline samples of Mn 0, Mn 38, Mn 57 and Mn 76 in a vacuum arc melting furnace under a high-purity argon atmosphere. The raw materials of Fe, Mn, Al, and La are all at least 99.9 wt % pure. An excess 10 % of La over the stoichiometric composition was added to compensate for the loss during melting. Button-like samples were melted four times, and each time buttons were melted ingots were sealed in a vacuum quartz tubes, followed by quenching at 950 °C for 10 days, and finally cooled down quickly to room temperature.

The linear thermal expansion data ($\Delta L/L$) were measured using a strain gage (gage factor: 1.74, type: BB120-2AA250) over the temperature range of 5 - 300 K. We have analyzed the crystal structure of the samples using X-ray diffraction (XRD) on a Bruker D8 advanced X-ray diffractometer with Cu K$_\alpha$ radiation (K$_{\alpha 1}$ = 1.5406 Å and K$_{\alpha 2}$ = 1.5443 Å). The angular scanning range was set to 20° to 80° with a step of 0.005° and scanning rate 0.5 s/step. The Fe$^4$-Fe$^4$ bond length was calculated by the first-principles geometry optimization calculation using CASTEP package. Measurements of magnetization at different temperatures were performed on the physical property measurement system (Quantum Design).

3. Results and discussion

3.1. Abnormal thermal expansion

The effect of Mn doping on abnormal thermal expansion (ATE) properties of the LaFe$_{11.4}$Al$_{1.6}$ compound was extensively explored based on their macro-strain. Figure 1(a) displays the linear thermal expansion $\Delta L/L$ data (reference temperature: 300 K) as a function of temperature for Mn 0, Mn 38, Mn 57 and Mn 76 in the temperature range from 5 K to 300 K. It has been reported that the Mn 0 material undergoes a slight increase with decreasing temperature from about 255 K to 150 K, and shows an excellent zero thermal expansion (ZTE) behavior below 150 K.[15] However, a sharp volume change can be found at relatively low temperatures by introducing Mn atoms, which indicates that large negative thermal
expansion (NTE) occurs. It is obvious that each \( \Delta L/L \) versus \( T \) curve with different Mn content presents different NTE operation-temperature windows and coefficients of thermal expansion, demonstrating that the NTE property of the LaFe\(_{11.4}\)Al\(_{1.6}\) compound can be effectively adjusted by optimizing Mn concentration. The coefficient of thermal expansion \( \alpha \) (CTE) is defined as \( (\Delta L/L)_T - (\Delta L/L)_{T1} / (T_2 - T_1) \) from the \( \Delta L/L \) versus \( T \) curves. For Mn 38, the value of the \( \Delta L/L \) increases with decreasing temperature from 50 K to 175 K, indicating the NTE behavior across a temperature range of \( \Delta T = 125 \) K (50 - 175 K) with a negative CTE calculated to be \(-11.38 \times 10^{-6} \) K\(^{-1}\). Furthermore, the temperature range is \( \Delta T = 145 \) K (5 - 150 K) for Mn 57 while it is \( \Delta T = 120 \) K (5 - 125 K) for Mn 76. Therefore, the NTE operation-temperature window decreases by increasing the amount of Mn. However, the average CTE slightly decreases as the increase of Mn content. The CTE is \(-6.23 \times 10^{-6} \) K\(^{-1}\) and \(-4.62 \times 10^{-6} \) K\(^{-1}\) for the samples of Mn 57 and Mn 76, respectively, which is significantly lower than that of the Mn 38 compound.

More fascinatingly, the NTE property can counteract the normal positive thermal expansion (PTE) to exhibit almost zero thermal expansion (ZTE) behavior. Figure 1(b) shows the temperature dependence of linear thermal expansion \( \Delta L/L \) data for Mn 0, Mn 57 and a mixture of Mn 0 and Mn 57 with equal amount. It was found that the ZTE can occur in the span of 150 - 255 K by combining the Mn 0 and Mn 57 materials. The origination of ZTE for the composite is specifically explained in the inset of Figure 1(b). In the certain temperature range 150 - 255 K, the Mn 0 compound shows a thermal expanding while Mn 57 gives rise to a thermal contraction due to the temperature decrease. Importantly, the volume expansion just compensates the volume contraction, thus the ZTE behavior can be observed and modified for a wider operation-temperature range.

**Figure 1.** (a) Temperature dependence of linear thermal expansion \( \Delta L/L \) (reference temperature: 300 K) from 5 K to 300 K for Mn 0, Mn 38, Mn 57 and Mn 76 compounds. (b) Temperature dependence of linear thermal expansion \( \Delta L/L \) data for the mixture of Mn 0 and Mn 57 with equal amount. The inset shows the ZTE behavior of the composite from 150 K to 255 K.

3.2. X-ray diffraction and crystal structure

Previous research has revealed that the Mn 0 compound crystallizes in a nearly single phase of the cubic NaZn\(_{13}\)-type structure (space group: \textit{Fm\textbar{3}c}).\cite{15} To explore the effect of Mn dopant on the crystal structure, the powder X-ray diffraction (XRD) patterns were obtained at room temperature, as shown in Figure 2(a). It can be found that the crystal structure of Mn 38, Mn 57 and Mn 76 remains cubic NaZn\(_{13}\)-type structure based on the dominant diffraction peaks of the 1:13 phase. In the inset of Figure 2(a), it can be seen that the lattice constant gradually decreases by the further substitution of Mn for Fe, in accordance with the smaller atomic radius of Mn than that of Fe. Furthermore, a small quantity of the
α-Fe phase can be observed calculated to be less than 0.93 wt % and has a negligibly minor effect on the overall ATE property.

The NaZn_{13}-type crystal structure of the Mn doped La(Fe, Al)_{13} compounds was shown in Figure 2(b). The Fe atoms are divided into Fe^I (8b) and Fe^II (96i) according to their different locations in the lattice. Moreover, Mn atoms only enter the 96i sites substituting Fe^II randomly. Therefore, the sites of 8a, 8b and 96i are occupied by the atoms of La, Fe^I and (Fe^II/Al/Mn), respectively. Here, the atom of Fe^I has an fcc-like local environment surrounded by 12 nearest neighbors, and the interatomic plays a significant role in the magnetic exchange interaction. In other words, when the distance of the Fe^I-Fe^II pair is smaller than 2.45 Å, the exchange interaction is negative while the interaction is positive at larger Fe^I-Fe^II distances. For La(Fe_{1-x}Mn_x)_{11.4}Al_{1.6} compounds, the average Fe^I-Fe^II distance is 2.38186 Å, 2.38314 Å and 2.39678 Å for Mn 38, Mn 57 and Mn 76, respectively. Hence, the decrease of the NTE operation-temperature window can be explained by the substitution of Mn for Fe, which leads to the increase of the Fe^I-Fe^II distance and decreases the exchange interaction.

![Figure 2](image)

Figure 2. (a) XRD patterns for Mn 0, Mn 38, Mn 57 and Mn 76 compounds. The inset shows the lattice constant for the compounds. (b) NaZn_{13}-type structure (space group: Fm\overline{3}c) of the compounds with partial substitution of Mn for Fe.

3.3. Magnetic properties and mechanism study

Figure 3(a) presents the temperature dependence (5 - 300 K) of the magnetization M(T) for all the samples measured in a magnetic field of 0.1 T. It was reported that the Mn 0 compound shows a second-order transition from the antiferromagnetic (AFM) to the paramagnetic (PM) state as the temperature reach the Neel temperature T_N.\textsuperscript{15} However, distinctly different with Mn 0, a sharp magnetization change can be observed with the increase of temperature for Mn 38, Mn 57 and Mn 76, indicating that a ferromagnetic (FM) to PM transition occurs. The Curie temperature (T_C) was determined with the smallest rates of change of the magnetization (dM/dT) value from dM/dT curves, as shown in Figure 3(b). It is obvious that the T_C moves towards the lower temperature with more Mn atoms inserted into the lattice. Compared with the NTE property shown in Figure 1, we found that the NTE just occurs around the T_C, which is 140 K, 110 K and 90 K for Mn 38, Mn 57 and Mn 76, respectively. Therefore the decrease of the T_C makes the NTE behavior moving to low temperatures due to the weak coupling between magnetic transitions. Moreover, the decrease of average CTE as the increase of Mn content may be due to the decrease of the intensity of magnetization in the low-temperature FM state. Such optimization makes these ATE materials to be promising candidates for broader application in low temperature sensitive equipment and devices.
Figure 3. (a) Temperature dependence (5 - 300 K) of magnetization $M(T)$ for Mn 0, Mn 38, Mn 57 and Mn 76 compounds measured under a field of 0.1 T. (b) The rate of change of magnetization as a function of temperature for Mn 38, Mn 57 and Mn 76 compounds.

4. Conclusion

In summary, we have investigated the effect of Mn doping on ATE property for NaZn$_{13}$-type Mn 0, Mn 38, Mn 57 and Mn 76 compounds. The results reveal that the NTE operation-temperature window decreases from $\Delta T = 105$ K (150 - 255 K) to $\Delta T = 120$ K (5 - 125 K) by introducing Mn atoms, and such a low temperature window with the NTE property makes the Mn doped samples suitable for practical applications in low temperature sensitive equipment and devices. Furthermore, the composite combining Mn 0 and Mn 57 broadens the ZTE behavior occurring in the whole tested temperature range. Magnetic measurements show that the ATE property is mainly correlated with the magnetic phase transition. The ATE discovery of Mn doped La(Fe, Al)$_{13}$ compounds at low temperature would improve their potential applications in cryogenic engineering.

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