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Phase, structural, and magnetocaloric properties of high temperature annealed $LaFe_{11.6}Si_{1.4}B_X$

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ABSTRACT

The phase relation, microstructural, hysteresis, Curie temperature, and magnetocaloric effects of $LaFe_{11.6}Si_{1.4}B_x$ (x = 0.1, 0.2, 0.3, 0.4, and 0.5) prepared by arc-melting and then annealed at 1373 K (1.5 h) + 1523 K (5 h) were investigated. It was found that the main phase is $NaZn_{13}$-type phase, the impurity phases include α-Fe, Fe_2B, and small amount of La_5Si_3. The boron atom can dissolve into the crystal lattice of $LaFe_{11.6}Si_{1.4}B_x$ to form interstitial solid solution, but the content of solid solution is not up to x = 0.5. For $LaFe_{11.6}Si_{1.4}B_x$ (x = 0.1, 0.3, and 0.5) compounds, the Curie temperature T_C increases from 190.6 to 198.3 K with the increasing of B content from x = 0.1 to 0.5. The first order magnetic transition behavior becomes weaker and magnetic entropy change ΔS_M (T, H) drops with the increasing of B content, respectively. However, ΔS_M (T, H) still remains a large value, 11.18 J/kg K, when x reaches to 0.5 at 0–2 T. An attractive feature is that both thermal and magnetic hysteresis can be reduced remarkably by introducing B. The maximum magnetic hysteresis loss near T_C drops from 22.52 to 4.95 J/kg when the content of B increases from x = 0.1 to 0.5.

1. Introduction

Magnetic refrigeration can be realized by utilizing the heat released or absorbed of a magnetic material due to a magnetic field change ΔH [1]. It is becoming a promising technology to replace the conventional vapor-cycle refrigeration. Since 1997, Pecharsky and Gschneidner discovered the giant magnetocaloric effect (GMCE) in $Gd_5(SixGe_{1-x})_4$ alloys with the first magnetic transition [2,3], materials with a first-order magnetic phase transition such as $LaFe_{13-x}Si_x$, $MnFeP_{1-x}As_x$, $MnAs_{1-x}Sb_x$ have been intensively investigated[4–12]. Those alloys have magnetoelastic coupling or magnetovolume coupling characteristic, i.e the magnetic transition between paramagnetic and ferromagnetic occurs accompanied by the change of the crystal structure or crystal constant at the same time. They are of prime interest as they show giant magnetic entropy changes.

Comparing with the other giant magnetocaloric effect alloys, $LaFe_{13-x}Si_x$ alloys have the advantages such as the lower price of starting materials, giant magnetic entropy change and adjustable Curie temperature T_C with the addition of hydrogen or cobalt etc [13–18]. However, the compounds are not directly suitable for room temperature application as its ordering temperature T_C is around 200 K. In order to work as a magnetic refrigerant near the ambient temperature, it is needed to adjust T_C to room temperature while retaining its large magnetic entropy change. In addition, materials with the first-order magnetic transition including $LaFe_{13-x}Si_x$ alloys have the large magnetic hysteresis loss, which makes magnetic refrigeration less efficient [19–21]. To improve the efficiency of magnetic refrigeration, it is necessary to depress the hysteresis loss. Hydrogen, nitrogen, carbon, and boron atoms, introduced as interstitial atoms, affect the magnetic properties by lattice expansion and hybridization [22–25]. It has been reported that boron has large content of dissolving in the crystal lattice of $LaFe_{13-x}Si_x$ to form interstitial solid solution, even up to 1.64 in $LaFe_{11.57}Si_{1.43}B_x$ compounds [26]. T_C has been considerably increased in borides of $LaFe_{13-x}Si_x$ by B atoms without much affecting its interesting magnetocaloric properties, the magnetic hysteresis loss reduced almost to zero [25,26]. In this paper, boron has been incorporated in $LaFe_{11.6}Si_{1.4}$ by arc melting and then annealing at 1373 K (1.5 h) + 1523K(5 h). Phase, structural, thermal and magnetic hysteresis, and magnetic properties are studied in order to compare with the result obtained by long time annealing in previous studies.

2. Experimental

Approximately 10 g polycrystalline $LaFe_{11.6}Si_{1.4}B_x$ (x = 0.1, 0.2, 0.3, 0.4, and 0.5) buttons were fabricated by conventional arc melting in a high purity argon

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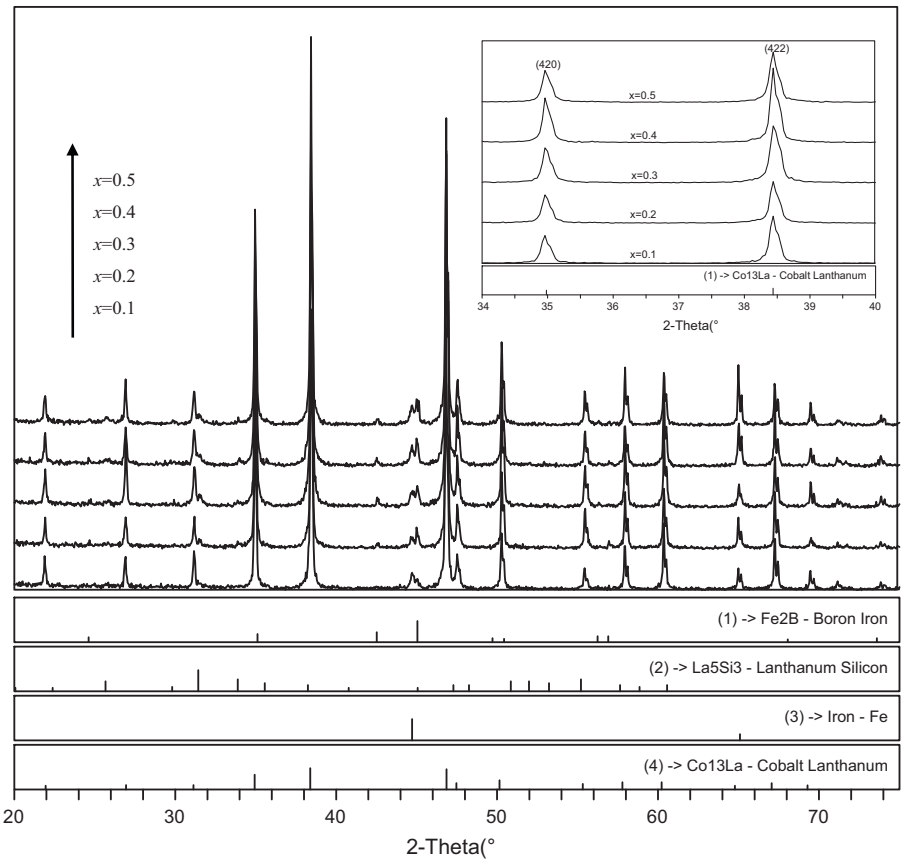

Fig. 1. XRD patterns of $LaFe_{11.6}Si_{1.4}B_x$ ($x = 0.1$, 0.2, 0.3, 0.4, and 0.5) compounds. The Inset shows the (4 2 0) and (4 2 2) diffraction peaks of $NaZn_{13}$-type phase.

atmosphere using high purity (La: 99.4%, Fe: 99.9%, Si: 99.9999%, and B: 99.9%) elements, the compounds were re-melted five times to achieve a homogeneous composition. The as-cast compound was annealed at 1373K(1.5 h) + 1523K(5 h), in a molybdenum wire furnace of 3×10^{-3} Pa vacuum, followed by furnace cooling down to room temperature. The phases and crystal structures were determined by powder x-ray diffraction (XRD) using Cu (K_α) radiation. The microstructural analysis was carried out by SEM with EDS attached, model Hitachi- S-3400N. Magnetic measurements were performed by using a vibrating-sample magnetometer (VSM, Lakeshore 7410) with a maximum field of 2 T. The Curie temperatures (T_C) were determined from the maxima of dM/dT of the M–T curves and were measured in an applied magnetic field of $H = 0.02$ T. The magnetic entropy changes ΔS_M (T, H) were calculated from isothermal magnetization curves (M–H curves) in the vicinity of the Curie temperature by using the thermodynamic Maxwell relation according to Eq. (1) [27]. The isothermal magnetization curves

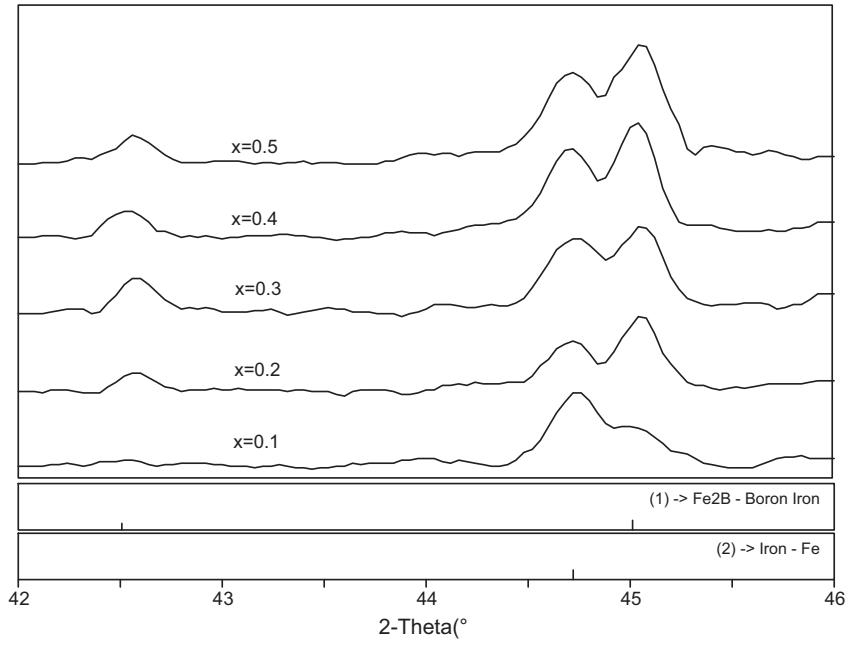

Fig. 2. Partial XRD patterns of $LaFe_{11.6}Si_{1.4}B_x$ ($x = 0.1$, 0.2, 0.3, 0.4, and 0.5) compounds from $2\theta = 42^\circ$ to 46°.

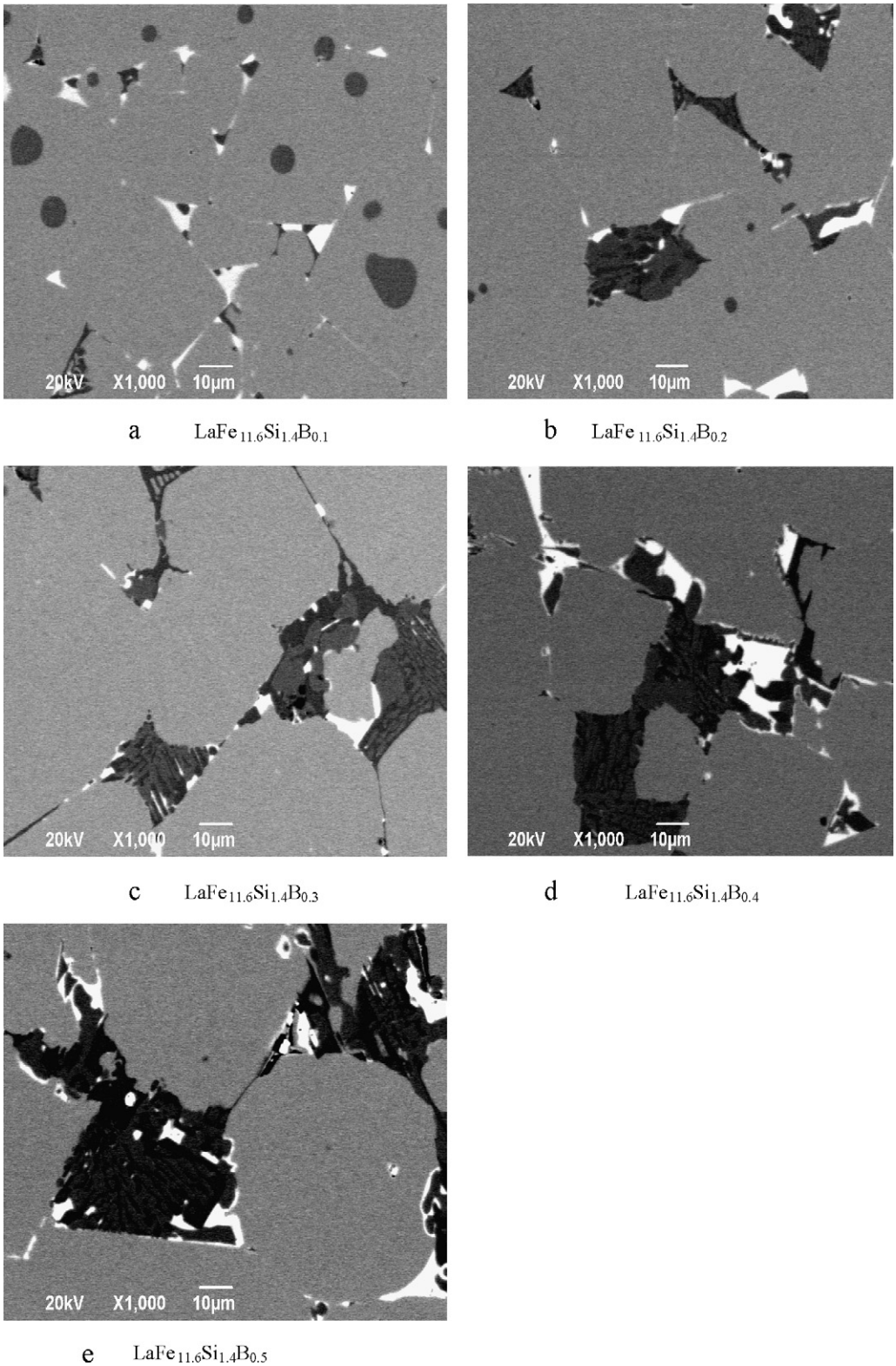

Fig. 3. Backscattered SEM micrographs of $LaFe_{11.6}Si_{1.4}B_x$ (x = 0.1, 0.2, 0.3, 0.4, and 0.5) compounds.

were measured in a temperature range of 150-300 K, and in magnetic fields up to 2 T. For magnetization measured at discrete field and temperature intervals, the magnetic entropy change defined in Eq. (1) can be approximated by Eq. (2) [28].

$$\Delta S_M(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \quad (1)$$

$$\Delta S_M(T,H) = \frac{1}{\Delta T}\left[\int_0^H M(T+\Delta T,H)dH - \int_0^H M(T,H)dH\right] \quad (2)$$

3. Results and discussion

According to our recent work about the effect of different high-temperature and short-time annealing from 1323 K to 1623 K on

$LaFe_{11.6}Si_{1.4}$ compound, we found that 1523 K is a critical temperature, the LaFeSi phase is rarely observed in the XRD pattern and the most amount of 1:13 phase can be obtained when the as-cast $LaFe_{11.6}Si_{1.4}$ compound was annealed at 1523 K (5 h) and then cooling down to room temperature. The 1:13 phase is formed from a peritectoid or peritectic reaction between the Fe and the LaFeSi phase during the annealing of as-cast compound. From the angle of thermodynamics, the more degree of super-cooling or the lower temperature is, the larger chemic driving force of phase transition is in phase transition process. On the contrary, from the angle of kinetics, the higher the annealing temperature is, the larger the coefficient of diffusion and the kinetics of phase tranition are. Combining the result of the effect of different high-temperature and short-time annealing on $LaFe_{11.6}Si_{1.4}$ compound with the traditional preparing method that the as-cast $La(Fe,Si)_{13}$ compound was annealed at about 1373 K for long time. The $LaFe_{11.6}Si_{1.4}B_x$ compounds were prepared by two-stage annealed at 1373 K (1.5 h) +1523 K (5 h). The aim of annealing of low temperature (1373 K) and high temperature (1523 K) is increase the chemic driving force and diffused driving force of phase transition, respectively.

Fig. 1 shows the X-ray diffraction (XRD) patterns of the $LaFe_{11.6}Si_{1.4}B_x$ compounds collected at room temperature with $x = 0.1$, 0.2, 0.3, 0.4, and 0.5, respectively. By analyzing and indexing the X-ray diffraction patterns of samples using jade 5.0 software, one can find that the samples consist of the cubic $NaZn_{13}$-type main phase and small amount impurity phases. The inset in the Fig. 1 is the diffraction peaks of (4 2 0) and (4 2 2) crystal surface of the cubic $NaZn_{13}$-type structure phase, one can see that the peaks of five samples shift slightly to low angle with the increase of B content. The crystal cell parameters were found increasing from 11.465(1) to 11.468(4) Å, with $x = 0.1$ and 0.5, respectively. Those indicate that B atoms can dissolve into the lattice or substitute the matrix atoms of the compound to form solid solution, and the content of solid solution raises with the increase of B in $LaFe_{11.6}Si_{1.4}B_x$ compounds. But concerning with whether or not all B element can enter into crystal lattice interstice of 1:13 phase to form interstitial solid solution, our result is different to some previous result, which showed that B atoms can dissolve into the lattice or substitute other atoms to form interstitial solid solution and the range of solid solution is large [25,26], even to $x = 1.64$ in $LaFe_{11.57}Si_{1.43}B_x$ compounds, and indexed the diffraction peaks of about $2\theta = 44.7^\circ$ and $2\theta = 45^\circ$ as peaks of α-Fe phase. From Fig. 2, one can see that the ratio between the two diffraction peaks has obvious change with the B increase. It indicates peaks of $2\theta = 44.7^\circ$ and 45° are two different phases' diffraction peaks. By indexing, they are the peaks of α-Fe and Fe_2B phases, respectively. It indicates that not all B elements have entered into crystal lattice interstice of 1:13 phase to form interstitial solid solution and part reacts with Fe atoms to form Fe_2B phase, the solid solution range of B in $LaFe_{11.6}Si_{1.4}B_x$ is not up to $x = 0.5$ in this work. With the increase of B content from $x = 0.1$ to 0.5, the Fe_2B phase also increases, it exhibits that the peak $2\theta = 45^\circ$ gradually becomes intensity with the B increase. In addition, five XRD patterns have a little peak at about $2\theta = 31.5^\circ$, this is the main peak of La_5Si_3 phase, i.e. the impurity phases consist of α-Fe, Fe_2B, and small amount of La_5Si_3 phase. Fig. 3 is scanning electron microscope (SEM) of five samples, there are four phases in all samples, this is accord with the XRD result. The analysis of energy disperse spectroscopy (EDS) indicates that the light gray phase is $NaZn_{13}$-type phase, the white phase is La_5Si_3, the deep gray phase is Fe, and the black phase is Fe_2B. From Fig. 3, one can find that the black phase (Fe_2B) gradually increase with the B increase in the SEM micrographs of $LaFe_{11.6}Si_{1.4}B_x$ compounds.

In $La(Fe,Si)_{13}$ systems with interstitial atoms, lattice expansion will lead to an increase of T_C because of the extension of Fe–Fe distance. An expansion of unit lattice in $La(Fe,Si)_{13}$ with interstitial B, H or C atoms causes a larger Fe–Fe distance [25,29,30], resulting in a stronger Fe–Fe exchange interaction, and then a shift of T_C to higher temperature. Fig. 4 displays the temperature dependent of magnetization measured under 0.02 T in heating and cooling processes for samples $x = 0.1$, 0.3, and 0.5, respectively. T_C is defined as the maximum of dM/dT on heating process. From Table 1, one can find that T_C increases from 190.6 to 198.3 K along with the increasing of B content from $x = 0.1$ to 0.5, and temperature hysteresis reduces. For the sample with $x = 0.1$, a thermal hysteresis of 3.4 K is observed around T_C, indicating the presence of a thermal induced first-order magnetic transition, and the thermal hysteresis is about 1.6 K in the samples with $x = 0.5$, implying that the incorporation of B weakens the first-order nature of the magnetic transition at T_C. In addition, the magnetization above T_C of $x = 0.5$ is larger than those $x = 0.1$ and 0.3, this can be attributed to the presence of the strong ferromagnetic impurity.

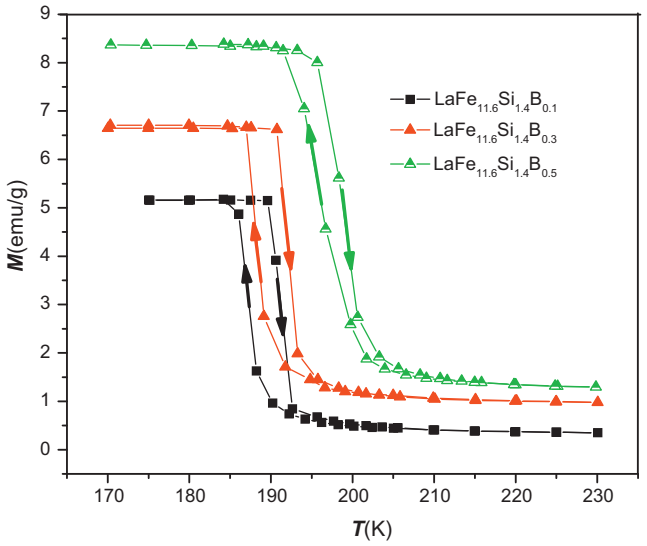

Fig. 4. Temperature dependence of magnetization measured under 0.02 T for $LaFe_{11.6}Si_{1.4}B_x$ ($x = 0.1$, 0.3, and 0.5) compounds.

The isothermal magnetization curves (M–H curves) measured at different temperatures in the vicinity of the Curie temperature under the magnetic field of 0–2 T are shown in Fig. 5 for $LaFe_{11.6}Si_{1.4}B_x$ ($x = 0.1$, 0.3, and 0.5) compounds. The measurements were performed in field increasing process. In order to check whether the isothermal magnetization process involves magnetic hysteresis, one of M–H curves were measured during the field up and down at near T_C. One can find that the M–H curves below T_C exhibit a characteristic of ferromagnetism for all samples. With increasing temperature above T_C, there is not an obvious field-induced itinerant-electron metamagnetic (IEM) transition from the paramagnetic state to the ferromagnetic state, especially for $x = 0.5$. It indicates that the critical field (H_C) of field- induced IEM transition is higher than 2 T. The observed nonlinear field dependence of magnetization at temperatures far above T_C is attributed to the α-Fe and Fe_2B phases, which is consistent with the XRD analysis.

Table 1
The crystal cell parameters, phase transition temperatures, maximum magnetic entropy changes $|\Delta S_{Max}|$, thermal hysteresis and magnetic hysteresis losses of $LaFe_{11.6}Si_{1.4}B_x$ ($x = 0.1$, 0.3, and 0.5) compounds.

x	a (Å)	T_C	$\lvert\Delta S_{Max}\rvert$ (J/kg K)	Thermal hysteresis (K)	Magnetic hysteresis (J/kg)
0.1	11.465(1)	190.6	15.4	3.4	20.5
0.3	11.466(3)	193.3	13.5	3.2	11.4
0.5	11.468(4)	198.3	11.2	1.6	5.0

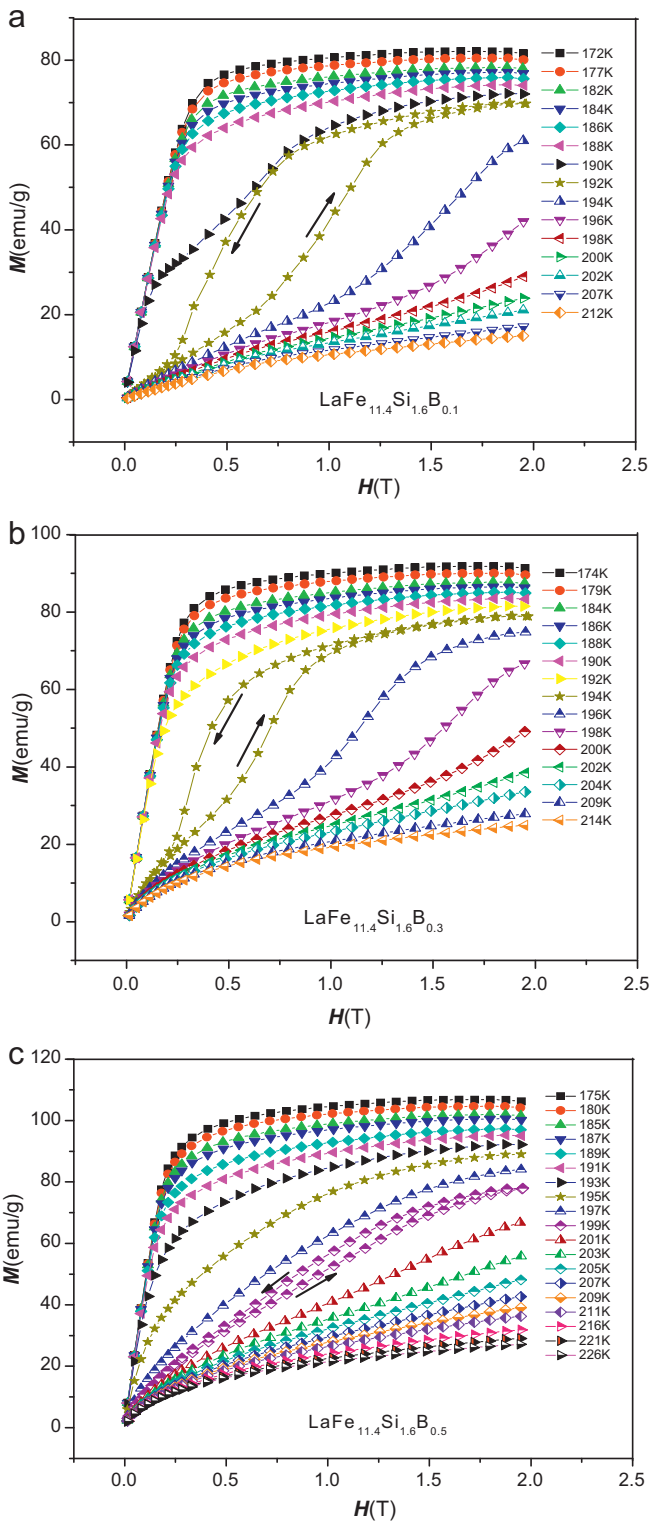

Fig. 5. Magnetization isotherms of $LaFe_{11.6}Si_{1.4}B_x$ ($x = 0.1$, 0.3 and 0.5) compounds measured under field of 0–2 T.

The hysteretic loss is defined as the enclosed area between the ascending and descending branches of magnetization curve. For $LaFe_{11.6}Si_{1.4}B_{0.1}$ compound, a large magnetic hysteresis occurs, the value of 20.52 J/kg appears at 192 K with $x = 0.1$ [see Fig. 5(a)]. When the increase of B content reaches $x = 0.5$, the magnetic hysteresis reduces to 4.95 J/kg at 199 K [see Fig. 5(c)], it indicates that the field-induced first-order transition from paramagnetic to ferromagnetic

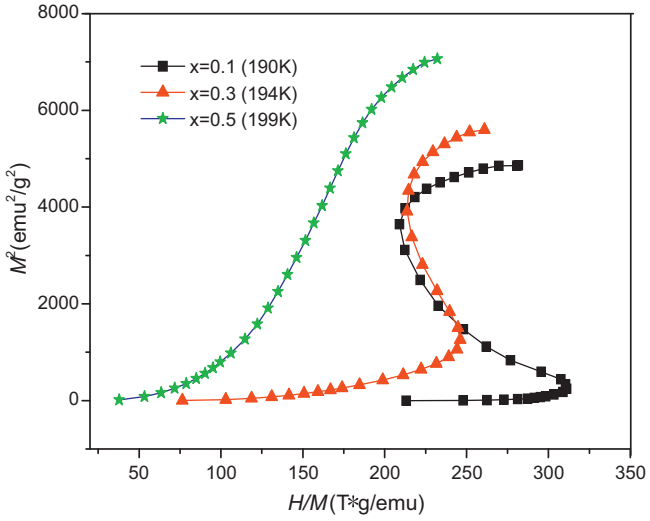

Fig. 6. Arrott plots of $LaFe_{11.6}Si_{1.4}B_x$ ($x = 0.1$, 0.3 and 0.5) compounds.

state was notably weakened upon introducing B. Fig. 6 shows the compared Arrott plots for samples $x = 0.1$, 0.3, and 0.5. One can find that negative slopes still appear even for sample $x = 0.5$, implying that a strong first-order magnetic transition behavior retains although the hysteresis loss becomes small. The strong first-order magnetic transition behavior with small magnetic hysteresis predicts a large almost reversible MCE effect. The decrease of hysteresis loss is very attractive for magnetic refrigeration technique.

Magnetic entropy change ΔS_M (T, H) was calculated by using Maxwell relation based on the magnetization data. Fig. 7 shows the ΔS_M (T, H) as functions of temperature and magnetic field for $LaFe_{11.6}Si_{1.4}B_x$ for compounds with $x = 0$, 0.3, and 0.5. Because the experimental field is lower than the H_C of field-induced IEM transition, ΔS_M (T, H) peaks have no obvious asymmetrical broad phenomenon to higher temperature at temperatures above T_C. The maximum ΔS_M (T, H) under 2 T magnetic fields are found to be 15.39 and 11.18 J/kg K for samples $x = 0.1$and $x = 0.5$, respectively. As a result of the increase of T_C, the ΔS_M (T, H) peak shifts toward higher temperatures. Although ΔS_M (T, H) exhibits a reduction in value, the maximum ΔS_M (T, H) in $LaFe_{11.6}Si_{1.4}B_{0.5}$ still attains 11.18 J/kg K for a field change of 0–2 T, and small magnetic hystere-

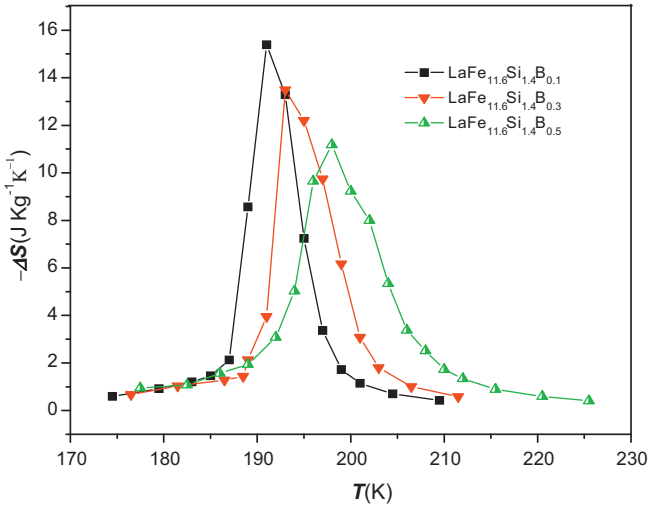

Fig. 7. Magnetic entropy change ΔS_M (T, H) as functions of temperature for $LaFe_{11.6}Si_{1.4}B_x$ ($x = 0.1$, 0.3, and 0.5) compounds under magnetic field of 0–2 T.

sis loss appears in this sample, it indicates an almost completely reversible MCE.

4. Conclusions

The samples of $LaFe_{11.6}Si_{1.4}B_x$ ($x = 0.1$, 0.2, 0.3, 0.4, and 0.5) were prepared by arc-melting and then annealing at 1373 K (1.5 h) + 1523 K (5 h). The phase relation, micorstructural, magnetic, and magnetocaloric properties of $LaFe_{11.6}Si_{1.4}B_x$ compounds have been investigated. The main phase is $NaZn_{13}$-type phase, the impurity phases include α-Fe, Fe_2B, and small amount of La_5Si_3. The boron atom can dissolve into the crystal lattice of $LaFe_{11.6}Si_{1.4}B_x$ to form interstitial solid solution, the crystal cell parameters and Curie temperatures were found increasing from 11.4651 to 11.4684 Å and 190.6 to 198.3 K, with $x = 0.1$ and 0.5, respectively. However, the content of solid solution is not up to $x = 0.5$, because the Fe_2B phase increases with increasing of B from $x = 0.1$ to 0.5. T_C shifted to higher temperature with the increase of B content which is attributed to the enlargement of Fe–Fe distance, resulting in a stronger Fe–Fe exchange interaction. Although the compounds exhibit a reduced $\Delta S_M(T, H)$ value, the maximum $\Delta S_M(T, H)$ still attains 11.18 J/kg K under 2 T when the B content increased to $x = 0.5$. The first-order nature of magnetic transition becomes weak with the increase of B content, resulting in a remarkable reduction in both thermal and magnetic hysteresis. The magnetic hysteresis loss at near T_C drops from 20.52 to 4.95 J/kg for $LaFe_{11.6}Si_{1.4}B_x$ with x varying from 0.1 to 0.5. These results will encourage further scientific exploration of these systems and the development of multifunctional applications.

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