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Effect of Pr and Co substitution on magnetic properties and magnetic entropy changes in $LaFe_{13-x}Si_x$ compounds

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Abstract

Effect of Pr and Co substitution on magnetic properties and magnetic entropy changes in the cubic $NaZn_{13}$-type compound $LaFe_{11.2}Si_{1.8}$ has been experimentally investigated. Replacing 30 at.% La with Pr leads to a decrease of Curie temperature from 216 to 203 K, and drives the magnetic transition from second-order to first-order. As a result, magnetic entropy change, under a field change of 0–5 T, increases from 13.7 to 19.4 J/kg K. Substitution of Co for Fe in $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ can adjust T_C to around room temperature. A magnetic entropy change of 9.3 J/kg K at $T_C = 290$ K for a field change from 0 to 5 T is obtained in $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$. A reversible variation of magnetization with temperature and magnetic field is observed in the present compound, which is highly desired by the magnetic refrigeration application.

Keywords: $LaFe_{13-x}Si_x$ compounds; Magnetic entropy changes; Magnetic properties

1. Introduction

La(Fe, $Si)_{13}$ compounds with a cubic $NaZn_{13}$-type structure show isotropic Heisenberg ferromagnetic and anomalous critical behavior [1]. Structure and magnetic properties for La(Fe, $Si)_{13}$ have been investigated systematically [2]. In recent years, much effort has focused on the magnetocaloric effect (MCE) of La(Fe, $Si)_{13}$ because of their potential application in magnetic refrigeration [3]. Previous investigations on $LaFe_{13-x}Si_x$ have confirmed that the compounds with $x < 1.7$ exhibit a first-order magnetic transition [4], which leads to a large magnetic entropy change [4–6] due to the itinerant electron metamagnetic (IEM) transition in the paramagnetic state above the Curie temperature T_C [7]. However, the Curie temperature is lower than ~208 K [5]. To meet the requirements of room-temperature magnetic refrigeration, it is necessary to adjust T_C to the room-temperature range while retaining the large magnetic entropy. It has been demonstrated that the large magnetic entropy change around room temperature can be gained by introducing Co or interstitial atoms into $LaFe_{13-x}Si_x$ [8–13]. Partially replacing La with Ce, Pr or Nd in La(Fe, $Si)_{13}$ was also found to significantly enhance magnetic entropy change [14–16]. In this paper, we report the effect of Pr and Co substitution on magnetic properties and magnetic entropy changes in $LaFe_{13-x}Si_x$ compounds with $x = 1.8$. A large magnetic entropy change and a reversible variation of the magnetization with temperature and magnetic field around Curie temperature are observed in the present compounds.

2. Experimental

Samples of $LaFe_{11.2}Si_{1.8}$, $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ were prepared by arc melting appropriate amounts of Pr (99%), La (99.9%), Fe (99.9%) and Co(99.9%), and Si (99.999%) in a high-purity argon atmosphere. The resulting ingots were wrapped by molybdenum foil, sealed in a quartz tube of high vacuum, annealed at 1373 K for 40 days and then quenched to room temperature. Powder X-ray diffraction (XRD) measurements were performed to check phase purity and structure. The magnetizations were measured as functions of temperature and magnetic field by using a superconducting quantum interference device magnetometer. The isothermal magnetic entropy change was calculated from the magnetization data by using the Maxwell relation.

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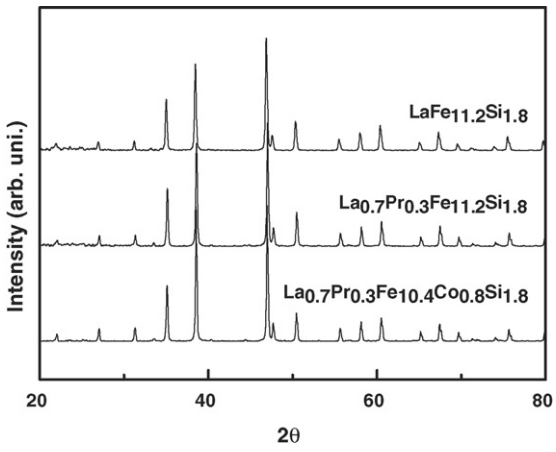

Fig. 1. Room-temperature powder XRD patterns of $LaFe_{11.2}Si_{1.8}$, $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$.

3. Results and discussion

Fig. 1 displays the room-temperature powder XRD patterns of $LaFe_{11.2}Si_{1.8}$, $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$. The compounds crystallized in a very clean single phase with a cubic $NaZn_{13}$-type structure. The lattice parameter, obtained from the XRD patterns, is 11.462 Å for $LaFe_{11.2}Si_{1.8}$, 11.451 Å for $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ and 11.453 Å for $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$. The substitution of Pr leads to a lattice contraction, as previously reported [14].

Fig. 2 shows the temperature dependence of magnetization for $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ (a) and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ (b) compounds measured in the heating and cooling processes under a field of 0.01 T. The temperature step of 1 K with a scanning rate of 1 K/min is chosen in the vicinity of T_C and a step of 5 K with a rate of 5 K/min for the regions far away from T_C. The thermomagnetic curve exhibits a discontinuous change at T_C. For the $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$, a small temperature hysteresis of 0.3 K is shown between the transition on heating and cooling, indicating the occurrence of a weakly thermal-induced first-order magnetic transition at T_C. It can be seen from Fig. 2 that

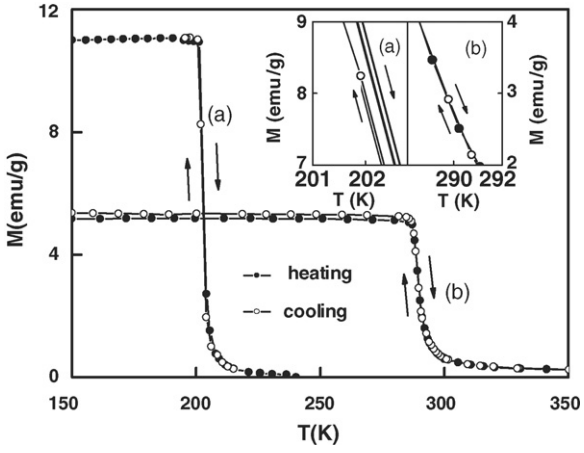

Fig. 2. Temperature dependence of the magnetization of $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ (a) and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ (b) measured on heating and cooling in a magnetic field of 0.01 T.

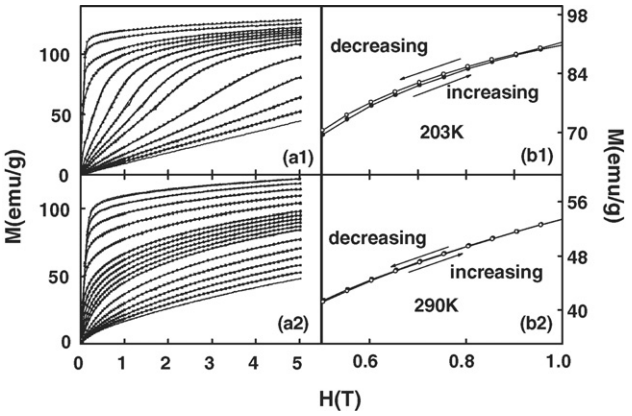

Fig. 3. Magnetization isotherms of $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ (a1) and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ (a2) on field increase and decrease. Isotherms on field increase and decrease are shown only at T_C in a field rang of 0.5–1 T for $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ (b1) and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ (b2).

$La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ shows a completely reversible variation of magnetization with temperature. This is a characteristic of second-order transition, as shown in $LaFe_{11.2}Si_{1.8}$ [17]. The Curie temperature T_C is 216, 203 and 290 K for $LaFe_{11.2}Si_{1.8}$, $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$, respectively. The substitution of Pr for La leads to a reduction of the T_C. A similar case is also observed in the Ce-doped $LaFe_{13-x}Si_x$ compounds [14], in which the substitution of Ce leads to the T_C to decrease. Substitution of smaller Pr atoms for La leads to the lattice contraction, which gives rise to weakening of the Fe–Fe interactions and the decrease of T_C. One can find that the substitution of Co for Fe in $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ can lift T_C to 290 K, near the room temperature. The obvious enhancement of T_C may result from the contributions of the strong Fe–Co interactions caused by substitution of Co for Fe.

Fig. 3a shows the magnetization isotherms of $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ measured in a wide temperature range around the Curie temperature and in the field ascending and descending processes, respectively. The temperature step of 2 K is chosen in the vicinity of T_C and a step of 5 K for the regions far away from T_C. For the samples of $LaFe_{11.2}Si_{1.8}$ [17] and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$, no magnetic hysteresis is observed, while the $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ compound shows a very small magnetic hysteresis at T_C as shown in Fig. 3b. This implies that the current samples show a nearly perfect magnetic reversibility, which is very favorable to magnetic refrigeration since a completely reversible MCE requires that there is no hysteresis in the magnetization as a function of both the temperature and the magnetic field. Fig. 4 shows the Arrott plots of $LaFe_{11.2}Si_{1.8}$, $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ compounds, in which a characteristic of second-order transition is shown for $LaFe_{11.2}Si_{1.8}$ and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ compounds. For $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$, an obvious inflection point in the Arrott plots at T_C is the signature of the IEM transition from paramagnetic to ferromagnetic order above T_C, which is expected for large magnetic entropy change. Such a behavior is consistent with that observed in the Ce doped $LaFe_{13-x}Si_x$ systems [14].

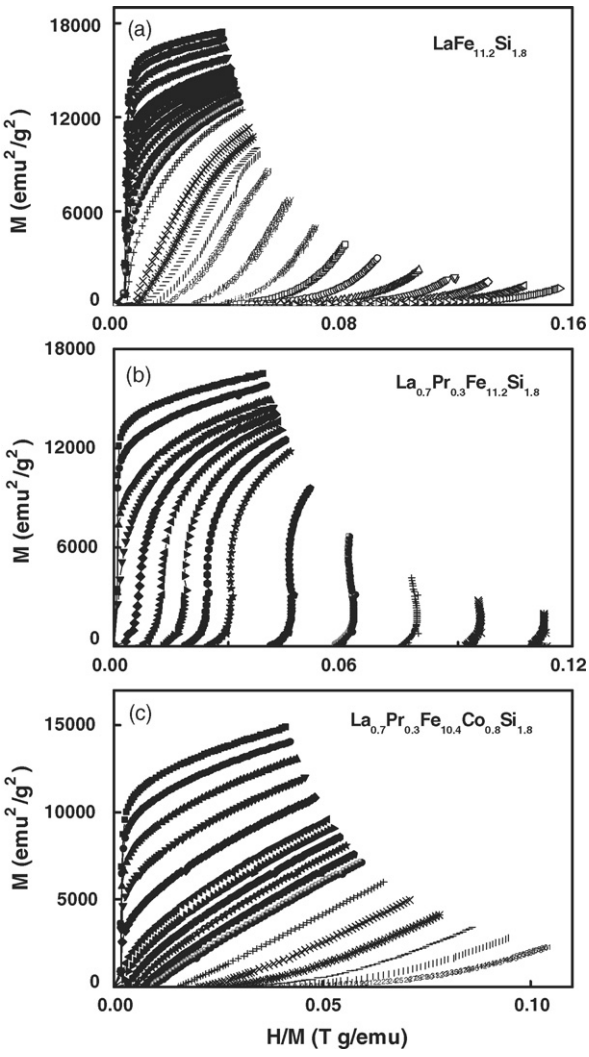

Fig. 4. Arrott plots of $LaFe_{11.2}Si_{1.8}$, $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$.

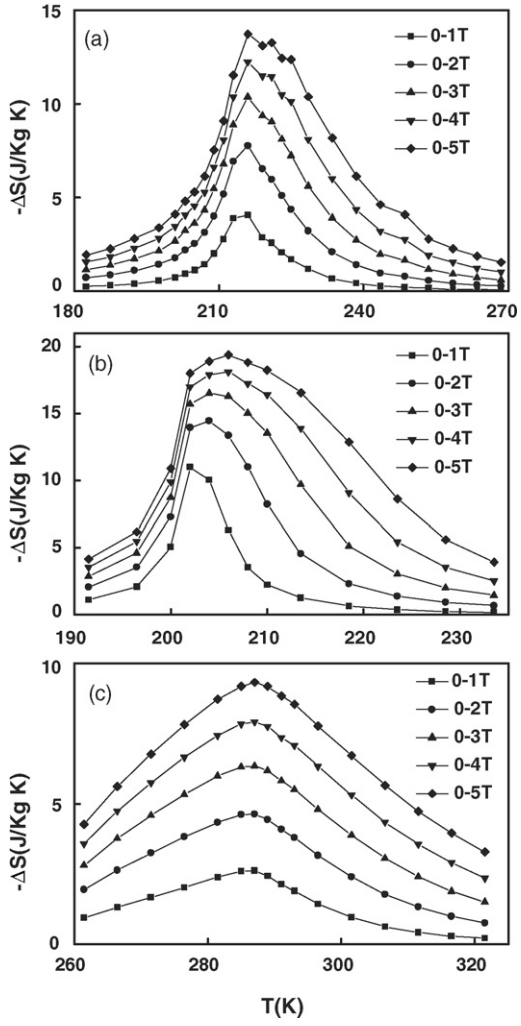

Fig. 5. Temperature dependence of the magnetic entropy change of $LaFe_{11.2}Si_{1.8}$ (a), $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ (b) and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ (c) for the magnetic field change of 0–1, 0–2, 0–3, 0–4 and 0–5 T.

The magnetic entropy change ΔS is calculated from magnetization data by using the Maxwell relation $\Delta S(T, H) = \int_0^H (\partial M/\partial T)_H \mathrm{d}H$. Fig. 5 shows the magnetic entropy change as a function of temperature for different magnetic field change. For the samples of $LaFe_{11.2}Si_{1.8}$, $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$, the maximum values of ΔS for a magnetic field change from 0 to 2 T and 0 to 5 T at T_C are found to be 7.8, 14.4, 4.6 J/kg K and 13.7, 19.4, 9.3 J/kg K, respectively. For the $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$, the maximum ΔS is 6.4 J/kg K larger than that of $LaFe_{11.2}Si_{1.8}$. The enhancement of ΔS is attributed to the occurrence of the field-induced IEM transition caused by substitution of Pr, which is demonstrated by the asymmetrical broadening of the ΔS peak under high applied field (see Fig. 5b). It is worthwhile to note that the maximum ΔS of the $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ is nearly as large as that of Gd, which has a ΔS value of 5.0 and 9.0 J/kg K at $T_C = 294$ K for a field change of 0–2 and 0–5 T [18], respectively. Therefore, the Co-doped $La_{1-x}Pr_xFe_{11.2}Si_{1.8}$ compounds are attractive candidates for magnetic refrigerants in an extended high-temperature range even at room temperature.

4. Conclusion

In summary, the room-temperature powder XRD patterns show that the $LaFe_{11.2}Si_{1.8}$, $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$ and $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ compounds crystallized in a very clean single phase with a cubic $NaZn_{13}$-type structure. The substitution of Pr for La in $LaFe_{11.2}Si_{1.8}$ leads to a reduction of the Curie temperature T_C. It is found that in $LaFe_{11.2}Si_{1.8}$ compound with a second-order magnetic transition, the substitution of Pr results in the occurrence of a field-induced IEM transition, which is required by large entropy change. For $La_{07}Pr_{0.3}Fe_{11.2}Si_{1.8}$, the maximum value of ΔS is found to 19.4 J/kg K at T_C in a magnetic field change from 0 to 5 T, which is 6.4 J/kg K larger than that of $LaFe_{11.2}Si_{1.8}$. Substitution of Co for Fe in $La_{1-x}Pr_xFe_{11.2}Si_{1.8}$ lifts T_C to room temperature, in the meantime driving the magnetic transition from first-order to second-order. The maximum value of ΔS for $La_{07}Pr_{0.3}Fe_{10.4}Co_{0.8}Si_{1.8}$ is 9.3 J/kg K at $T_C = 290$ K for a field change from 0 to 5 T, which is almost as large as that of Gd. It is worthwhile to point out that no obvious thermal and magnetic

hysteresis is observed, which is a promising feature of the present compounds.

Acknowledgements

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