Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF RARE EARTHS, Vol. 35, No. 7, Jul. 2017, P. 673
JOURNAL OF RARE EARTHS
www.re-journal.com/en/

Effect of proportion change of aluminum and silicon on magnetic entropy change and magnetic properties in $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ compounds

FU Bin (傅 斌)[1,*], HAN Jie (韩 洁)[2], WANG Chaolun (王超伦)[3]

(1. School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China; 2. College of Science, Tianjin University of Technology, Tianjin 300384, China; 3. Department of Electrical Engineering, East China Normal University, Shanghai 200241, China)

Received 24 September 2016; revised 16 January 2017

Abstract: The microstructure, magnetic entropy changes, hysteresis and magnetic properties of $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ (x=0.4, 0.5, 0.6, 0.7) compounds were studied by X-ray diffraction (XRD) and a superconducting quantum interference device magnetometer (SQUID). The results showed that all the compounds presented cubic $NaZn_{13}$-type structure. Their Curie temperatures changed complicatedly with decreasing Al content due to changes of antiferromagnetic and ferromagnetic interaction. Under a field change from 0 to 2 T, the maximum magnetic entropy change for $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.1}Si_{0.4}$, $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.0}Si_{0.5}$, $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{0.9}Si_{0.6}$ and $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{0.8}Si_{0.7}$ were found to be –9.6, –4.8, –5.8 and –11.7 J/(kg·K), respectively. Moreover, their hysteresis losses were 1.13 J/(kg·K) or less. The large magnetic entropy changed and small hysteresis losses made them potential candidates for practical magnetic refrigeration application.

Keywords: magnetic refrigeration; Curie temperature (T_C); magnetic entropy change; magnetocaloric effect (MCE); rare earths

The cubic $NaZn_{13}$-type $LaFe_{13}$-based compounds have attracted much attention in recent years due to their potential applications as magnetic refrigerants[1–6]. One of the current difficulties lies in finding magnetic refrigeration materials with both large entropy changes and small hysteresis. Magnetocaloric materials that show giant changes of entropy (GMCE) because of the underlying first order nature of the transition are of interest for application, but the associated hysteresis adds loss to the cooling cycle which restricts the use of magnetic refrigerator[7–12].

It was shown in previous researches that substitutions of other rare earth elements such as Pr, Ce and Nd for La increased magnetic entropy change (ΔS) due to enhanced first order behavior by increasing magnetic coupling between the rare earth and Fe in $LaFe_{13}$ compounds[13,14]. In these rare earth elements, the Ce partial substitution has a minimal influence on the formation of 1:13 phase[15]. On the other hand, the $La(Fe_{1-x}Al_x)_{13}$ compounds have a smaller hysteresis[15], and partial substitution of Si by Al reduced hysteresis obviously in $La(Fe_{1-x}Si)_{13}$ compounds[16]. Therefore, it should be an effective way to obtain pure $NaZn_{13}$-type structure phase and large magnetic entropy change while diminishing hysteresis loss by utilizing Ce substitution for La in $LaFe_{11.5}Al_{1.5-x}Si_x$ compounds.

For the sake of finding an appropriate composition with high cooling power and small hysteresis loss, in the present work, we prepared $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ compounds with x=0.4, 0.5, 0.6 and 0.7 and reported the effects of different proportion of Al and Si on the magnetic entropy change and magnetic properties in these materials. The structures, Curie temperatures, hysteresis and magnetic transition properties of the compounds were also investigated.

1 Experimental

Samples of $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ (x=0.4, 0.5, 0.6, 0.7) were prepared by arc melting method under a high purity argon atmosphere in water-cooled copper crucibles. The starting materials were pure (≥99.9%) elements, and excesses of 10% for La and Ce were used to compensate for the weight loss. All the arc-melted ingots were turned over and remelted at least three times to ensure their homogeneity. The resulting ingots were sealed under vacuum in quartz tubes and annealed at 1273 K for 10 d, and after that quenched in ice water. 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

Foundation item: Project supported by the Science and Technology Development Fund of Higher Education of Tianjin, China (20130301), the Tianjin Research Program of Application Foundation and Advanced Technology, China (14JCQNJC4000) and the National Natural Science Foundation of China (11604242)

* **Corresponding author:** FU Bin (**E-mail:** fubin80@126.com)

DOI: 10.1016/S1002-0721(17)60962-1

device magnetometer (SQUID). The isothermal magnetic entropy change was calculated from the magnetization data by using the Maxwell relation.

2 Results and discussion

Fig. 1 displays the room-temperature powder XRD patterns of $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ (x=0.4, 0.5, 0.6, 0.7). It shows that the main phase in all four compounds is cubic $NaZn_{13}$-type structure, additionally a very small amount of α-Fe is detected in $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{0.8}Si_{0.7}$ (indicated by an arrow). In Table 1, the lattice parameters, obtained from the XRD patterns, are 1.1630 nm (x=0.4), 1.1601 nm (x=0.5), 1.1579 nm (x=0.6) and 1.1503 nm (x=0.7). Because the ionic radius of Si is smaller than that of Al, the substitution of Si leads to a lattice contraction. And the contraction increases with increasing content of Si.

Shown in Fig. 2 are the thermomagnetization curves in a heating process under a magnetic field of 500 Oe for $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ (x=0.4, 0.5, 0.6, 0.7). The Curie temperatures of $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ compounds are 170 K (x=0.4), 174 K (x=0.5), 184 K (x=0.6) and 169 K (x=0.7), respectively.

Lattice parameters and Curie temperatures (T_C) as a function of Si content for $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ (x=0.4, 0.5, 0.6, 0.7) compounds are shown in Fig. 3. The lattice parameters decrease with Si content increasing as stated earlier, but Curie temperature T_C changes complicatedly with different proportions of Al and Si. In $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ compounds, there are superexchange antiferromagnetic interaction between Fe-Al atoms and ferromagnetic interaction between Fe-Fe atoms. With decreasing Al content, the antiferromagnetic interaction between Fe-Al atoms is weakened, which results in increasing of T_C. On the other hand, decreasing of unit cell volume with Al content decreasing leads to weakening of ferromagnetic interaction, and results in decreasing of T_C. Therefore, Curie temperature T_C increases and decreases with partial substitution of Al by Si result from joint two effects.

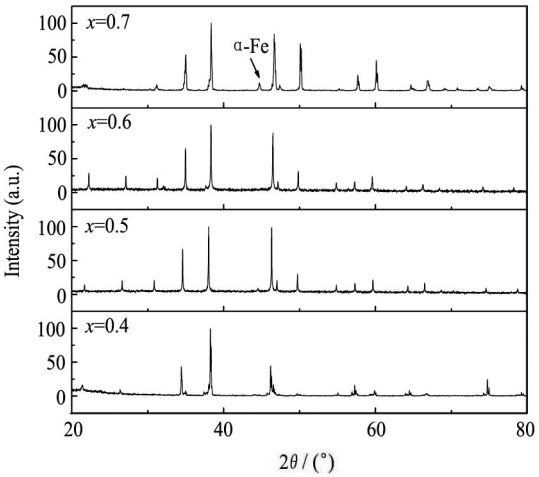

Fig. 1 XRD patterns of $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ (x=0.4, 0.5, 0.6, 0.7) compounds

Table 1 Lattice constants of $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ (x=0.4, 0.5, 0.6, 0.7)

Materials	Lattice constant a/nm
$La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.1}Si_{0.4}$	1.1630
$La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.0}Si_{0.5}$	1.1601
$La_{0.8}Ce_{0.2}Fe_{11.5}Al_{0.9}Si_{0.6}$	1.1579
$La_{0.8}Ce_{0.2}Fe_{11.5}Al_{0.8}Si_{0.7}$	1.1503

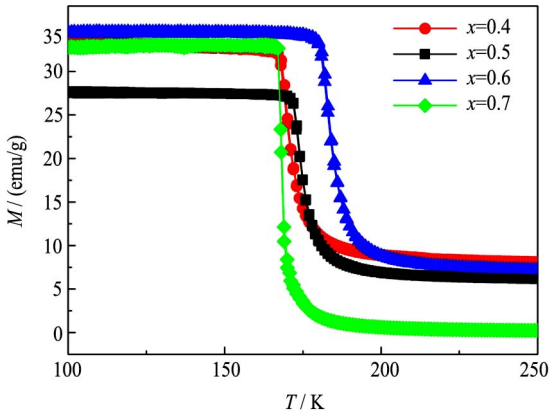

Fig. 2 M-T curves of $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ (x=0.4, 0.5, 0.6, 0.7) compounds

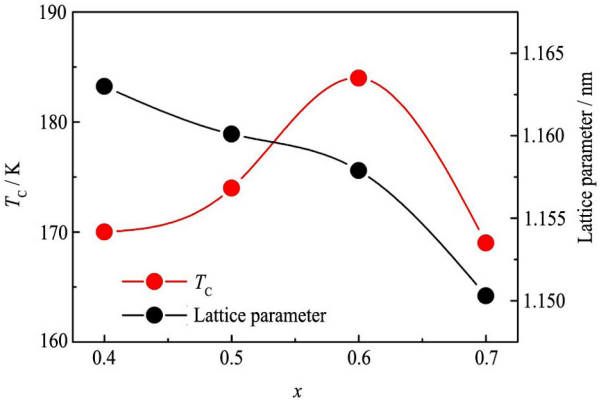

Fig. 3 Lattice parameters and Curie temperatures (T_C) as a function of Si content for $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ (x=0.4, 0.5, 0.6, 0.7) compounds

As examples, Figs. 4 and 5 give the magnetization curves and Arrott curves of $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.1}Si_{0.4}$ and $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{0.8}Si_{0.7}$, measured under increasing and decreasing field at various temperatures. The measurements are performed over a wide range of temperature around T_C. In Fig. 4(b), Arrott curves of compound show neither negative slope nor inflection point clearly, which means the phase transition of $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.1}Si_{0.4}$ compound is of second-order[17]. In Fig. 5(b), Arrott curves with negative slopes show that $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{0.8}Si_{0.7}$ compound undergoes typical first-order phase transition[17]. It can be seen from Fig. 4(b) and Fig. 5(b) that the replacement of Al by Si in $La_{0.8}Ce_{0.2}Fe_{11.5}Al_{1.5-x}Si_x$ has changed the slope from positive to negative and enhanced the characteristics of the itinerant-electron