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Influence of partial substitution of cerium for lanthanum on magnetocaloric properties of $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ and their hydrides

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Abstract: The structure and magnetocaloric properties of $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ and their hydrides $La_{1-x}Ce_xFe_{11.44}Si_{1.56}H_y$ (x=0, 0.1, 0.2, 0.3, 0.4) were investigated. The samples crystallized mainly in the cubic $NaZn_{13}$-type structure with a small amount of α-Fe phase as impurity. The lattice constants and Curie temperature presented the same change tendency with increasing of Ce content. For the hydrides, the influence of Ce content on lattice constants was weakened and the values of H concentration y were approximate to be 1.56. The $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ compounds exhibited large values of isothermal entropy change $-\Delta S_m$ around the Curie temperature T_C under a low magnetic field change of 1.5 T. The value of $-\Delta S_m$ increased and then decreased with increasing Ce content, reached the maximum, 26.07 J/kg·K for x=0.3. T_C increased up to the vicinity of room temperature by hydrogen absorption for the Ce substituted compounds, but T_C only slightly decreased with increasing Ce content. The first-order metamagnetic transition was still kept in the hydrides and the maximum values of $-\Delta S_m$ were lower than those of the $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ compounds, but still remained large values, about 10.5 J/kgK under a magnetic field change of 1.5 T. The values of $-\Delta S_m$ were nearly independent of the Ce content and did not increase with increasing x for the hydrides. The $La_{1-x}Ce_xFe_{11.44}Si_{1.56}H_y$ (x=0–0.4) hydrides exhibited large magnetic entropy changes, small hysteresis loss and effective refrigerant capacity covered the room temperature range from 305 to 317 K. These hydrides are very useful for the magnetic refrigeration applications near room temperature under low magnetic field change.

Keywords: $La_{1-x}Ce_xFe_{11.44}Si_{1.56}H_y$; isothermal entropy change; Curie temperature; magnetic hysteresis loss; rare earths

In the field of room temperature magnetic refrigeration, magnetic refrigerants with first-order phase transitions and large magnetocaloric effects (MCEs) play a key role. Several materials with giant MCEs have been discovered[1–4]. $LaFe_{13-z}Si_z$ compounds with the cubic $NaZn_{13}$-type structure belong to the most attractive magnetic refrigerants due to their advantages of giant MCEs, tunable Curie temperature T_C, low price of raw materials, excluding deleterious elements and easy preparation. So $LaFe_{13-z}Si_z$ based materials have been widely researched in recent years[5–10]. The particles of $La(Fe,Co,Si)_{13}B$ and the layered LaFeSiH system were used as magnetic refrigerants for direct testing on a room temperature magnetic refrigerator[11–13]. The layered LaFeSiH achieved significantly greater performance than the use of Gd metal under the same conditions. A high temperature recovery process can be used to solve the problem of the instability of LaFeSiH in magnetic refrigeration systems[12].

Recently, $LaFe_{13-z}Si_z$ compounds, in which La is partially replaced by the rare earth element Ce, have been investigated. It has been reported that the partial substitution of Ce for La resulted in the decrease of T_C as well as the enhancement of isothermal entropy change $-\Delta S_m$ for $LaFe_{13-z}Si_z$[14,15]. We investigated magnetocaloric properties of $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ (x is up to 0.4) and their hydrides. For $x\geq0.4$, the values of $-\Delta S_m$ do not increase with increasing Ce content x due to the structure changed[16]. In Ref. [17], the authors found that the MCEs of $La(Fe_{0.90}Si_{0.10})_{13}$ were enhanced by a partial substitution of Ce for La and this enhancement maintained in the vicinity of room temperature after hydrogen absorption. One knows that the hydrogen absorption can adjust Curie temperature T_C to around room temperature and leads to a decrease of isothermal entropy change $-\Delta S_m$ and magnetic hysteresis loss because the field-induced itinerant-electron metamagnetic (IEM) transition is weakened[18]. So we explored it by further experiments in this paper. On the other hand, $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ compounds exhibit giant MCEs under low magnetic field

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and their T_C can be turned to near room temperature by hydrogenating. So, industrially pure mixed rare-earth LaCe alloy can be used to prepare $La_{1-x}Ce_xFe_{13-z}Si_z$ magnetic refrigerants and the cost of refrigerants preparation is reduced which can be good for the development of room temperature magnetic refrigeration.

1 Experimental

The $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ (x=0, 0.1, 0.2, 0.3, 0.4) compounds about 100 g respectively were prepared by high frequency melting in the protection of high purity argon atmosphere. The as-cast compounds were annealed at 1473 K for 30 h in the vacuum sintering furnace filled with high purity argon atmosphere. The hydrogenation was carried out at 553 K under high purity hydrogen gas atmosphere of 0.2 MPa for about 5 h. The phase, crystal structures and the lattice constant were determined by powder X-ray diffraction (XRD) using Cu Kα radiation (PANalytical X'pert Pro). Thermo-gravimetric (TG) measurements were carried out by a simultaneous thermal analyzer instrument (NETZSCH STA449C) for obtaining the hydrogen concentrations. Magnetic measurements were performed by using a vibrating-sample magnetometer (VSM, LakeShore 7407). The Curie temperature T_C was identified as the minima in the first derivative of the M-T curve, which was measured under an applied magnetic field of 0.05 T. By using the Maxwell relation, the isothermal entropy change was estimated from the magnetization data measured in the vicinity of the Curie temperature at intervals of 2 K and the magnetic field step of 0.05 T from 0 to 1.5 T.

2 Results and discussion

2.1 Analysis of XRD and TG curves

XRD patterns of the $La_{1-x}Ce_xFe_{11.44}Si_{1.56}H_y$ compounds with x=0, 0.1, 0.2, 0.3, and 0.4 collected at the room temperature are shown in Fig. 1. It can be seen that the main phase is cubic $NaZn_{13}$-type structure (with the lattice constants of a=b=c and α=β=γ=90°) for all the samples with a small amount of α-Fe phase as an impurity phase. XRD patterns of the $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ compounds (not shown here) have the same diffraction peaks except the peaks of the $NaZn_{13}$ structure shift slightly to the large angle with the increase of Ce content which show that the partial substitution of Ce for La leads to decrease of the lattice constant. After hydrogen absorption, the peaks of the $NaZn_{13}$ structure shift clearly to lower angles which show that the lattice constant increased greatly. Fig. 2 displays the lattice constant a as a function of Ce content x for $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ compounds and their hydrides. For $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ compounds, the lattice constants decrease with increasing x

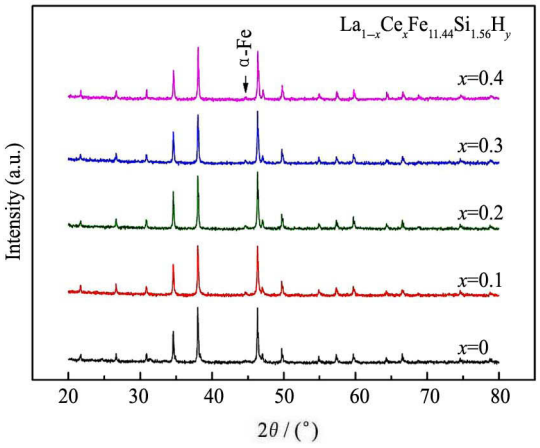

Fig. 1 XRD patterns of $La_{1-x}Ce_xFe_{11.44}Si_{1.56}H_y$

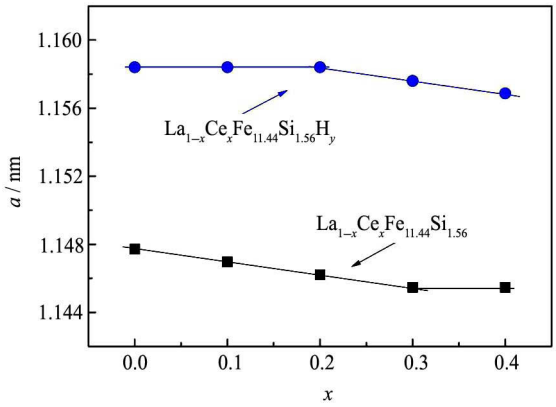

Fig. 2 Lattice constant as a function of Ce content for $La_{1-x}Ce_xFe_{11.44}Si_{1.56}$ and their hydrides (solid lines are guides for the eyes)

because the atomic radius of Ce is less than the atomic radius of La. For hydrides, the change of lattice constants is not obvious and the influence of Ce content on lattice constants is weakened. After hydrogen absorption, the lattice constants increase clearly, for example, a increases from 1.1462 to 1.1584 nm for x=0.2 and the unit-cell volume increases from 1.5058 to 1.5544 nm^3 (with volume expansion of 3%). In order to determine the H concentrations of the hydrides, TG curves have been measured. Fig. 3 shows the TG curve of the $La_{0.9}Ce_{0.1}Fe_{11.44}Si_{1.56}H_y$, the H concentration y is determined to be ~1.56. The other hydrides have the similar

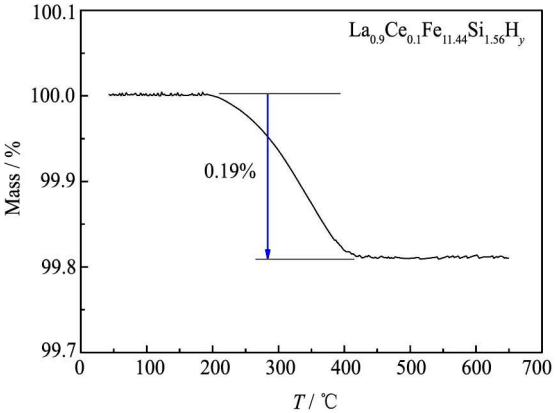

Fig. 3 TG curve of $La_{0.9}Ce_{0.1}Fe_{11.44}Si_{1.56}H_y$