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Magnetocaloric effect of $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ compounds

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ABSTRACT

The effect of Mn addition on the magnetocaloric effect (MCE) of the $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ ($x = 0.0$, 0.1, 0.2, 0.3) compounds was investigated. It was revealed that the transition temperatures of the compounds are sensitive to Mn composition. The temperatures are shifted from 177 to 121 K for Mn composition from 0.0 to 0.3. Moreover, thermal lag and magnetic hysteresis loss of the compounds are reduced largely due to Mn addition. A good MCE with a large and almost constant refrigerant capacity in a large temperature span over 50 K was achieved in the investigated compounds. The investigated compounds are promising magnetic entropy change materials.

1. Introduction

With the increase of air pollution, an environment-friendly magnetic refrigeration technology has drawn an increasing attention. This technology has various advantages over conventional vapor-cycle refrigeration, such as high efficiency, small volume, and ecological cleanliness. Recently, $La(FeSi)_{13}$ compounds as promising refrigerants exhibit large MCE with a first-order phase transition near the transition temperature [1–5]. Recent investigations revealed that partially replacement of La by Ce, Pr, Nd or Gd in $La(FeSi)_{13}$ compounds gives rise to a remarkable enhancement of MCE, and the substitution of Co for Fe results into an increase of Curie temperature (T_c) [6–13]. However, with the increase of T_c, the magnetic entropy change reduces evidently [13–16]. On the other hand, materials with the first-order phase transition exhibit a larger thermal lag and magnetic hysteresis loss [16–20], which deteriorate the MCE of materials. Consequently, it is important to obtain high MCE and to reduce the thermal lag and magnetic hysteresis loss.

In this paper, the effect of Mn addition on the MCE, thermal lag and magnetic hysteresis loss was investigated in $NaZn_{13}$-structured $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ compounds.

2. Experimental

$La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ ($x = 0.0$, 0.1, 0.2, 0.3) ingots were prepared using high-purified raw materials by arc melting in a high-purity argon atmosphere. Additional La, Ce and Mn were appended to make sure the compounds compositions close to the nominal ones as above. The resulting ingots were cut into pieces and sealed in a quartz tube under a vacuum atmosphere. The sealed samples were annealed at 1373 K for 5 days and subsequently quenched by cool water. The microstructure was identified by the X-ray diffractometer (XRD) with Cu Kα radiation. Magnetic properties were measured by a Versalab magnetometer (Versalab free, Quantum Design Co.).

3. Results and discussions

Fig. 1 showed XRD patterns of the series $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ ($x = 0.0$, 0.1, 0.2, 0.3) samples. As illustrated, all samples are mainly composed of a cubic $NaZn_{13}$-type phase. The lattice parameters, calculated using Scherrer equation, are slightly expanded from 11.4565, 11.4574, 11.4587 to 11.4600 Å for samples with Mn composition from 0.0 to 0.3, respectively. This fact demonstrated that Mn atoms enter the lattice positions since Mn radius is lager than Fe. In addition, small amount of α-Fe and LaFeSi phases are present in the compounds, analog to the report in Ref. [19].

Fig. 2 shows the M–T curves of $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ ($x = 0.0$, 0.1, 0.2, 0.3) compounds measured in the heating and cooling processes under a magnetic field of 0.1 T. It reveals that: (1) T_c is sensitive to Mn composition. The increase of Mn composition gives rise to a reduction of T_c. (2) The heating and cooling M–T curves do not superpose, indicating a thermal lag in the samples.

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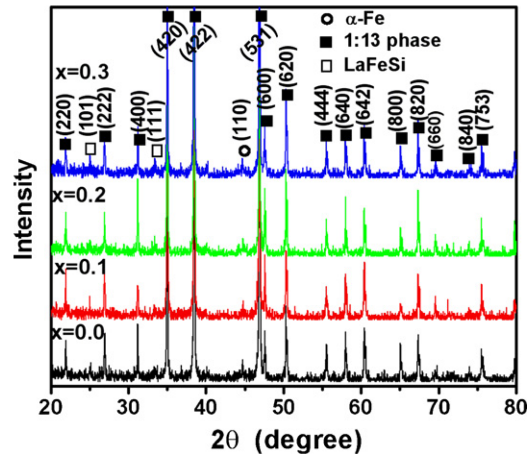

Fig. 1. XRD traces of $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ (x = 0.0, 0.1, 0.2, 0.3) compounds.

The magnetic order transition temperature is sensitive to the conducting electron density, which can be explained by the composition dependence between the magnetization transition temperatures and the values of e/a [21]. Since Mn atom has a lower conducting electron density than Fe atom, and the lattice constants of the series compounds were further expanded due to the Mn addition. Therefore, Mn addition must result in a decrease of d electron density, and a reduction of T_c as well [21]. On the other hand, the itinerant-electron metamagnetic (IEM) transition is related to the d electron band structure [19]. Mn hybridizes strongly with the 3d state of Fe, leading to a broadening of the sharp peak just below the Fermi level in the DOS of $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ compounds [19,22]. A reduction of the elastic energy change with Mn doped may be another possible reason of the gradual weakness of the IEM transition with increasing Mn composition [23]. A thermal lag around T_c similar to $La(FeSi)_{13}$ compounds evidently indicates that the $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ compounds are present the thermal-induced first-order transition.

The magnetic entropy change ΔS_M was calculated as a function of temperature and magnetic field from isothermal magnetization curves by the Maxwell relation as shown in Eq. (1)

$$\Delta S_M = \int_{H_1}^{H_2} \left(\frac{\partial M(H)_T}{\partial T} \right)_H \mathrm{d}H \tag{1}$$

The calculated results were shown in Fig. 3. As illustrated, the temperature spans are broadened with the increase of Mn

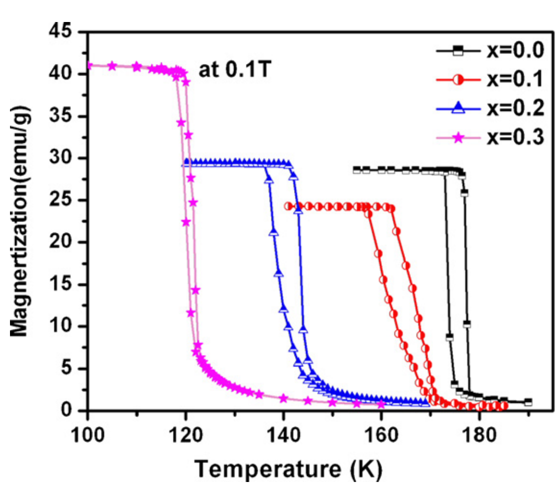

Fig. 2. M–T curves for $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ (x = 0.0, 0.1, 0.2, 0.3) compounds.

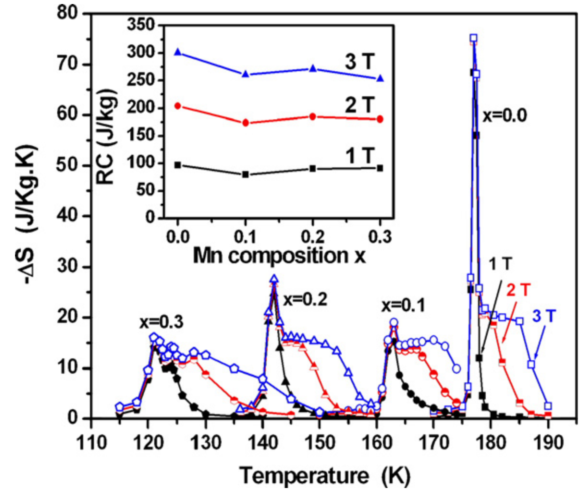

Fig. 3. Temperature dependence of magnetic entropy change of $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ (x = 0.0, 0.1, 0.2, 0.3) compounds, and their RCs at various fields (insert).

composition under various external fields, while the transition temperatures are shifted to lower values. The asymmetrical broad peaks of the ΔS_M were observed for various composition of Mn, which can be attributed to the field-induced IEM transition from paramagnetic to ferromagnetic state above T_c [24]. It was reported that an increasing external field may improve the order of inner atomic spin and reduce the minority spin, leading to the IEM property [22].

The refrigerant capacity (RC) for $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ (x = 0.0, 0.1, 0.2, 0.3) was calculated using Eq. (2). The RC, which refers to how much heat can be transferred from the cold end (T_1) to the hot end (T_2) of the refrigerator in one thermodynamic cycle, is defined as

$$\mathrm{RC} = \int_{T_1}^{T_2} \Delta S_M(T)_{\Delta H} \mathrm{d}T \tag{2}$$

The insert of Fig. 3 showed the calculated Mn composition dependence of RC at various fields. It is interested to note that the RCs are nearly independent on the Mn composition, while transition temperature changes from 121 to 177 K. In general, the variation of transition temperature in the MCE materials due to element addition is usually companied by a large change of magnetic entropy, as well as a change of RC. Moreover, the variations of transition temperature, magnetic entropy change and RC are sensitive to the composition of doping element. However, in the investigated compound system, when the Mn composition is changed from 0.0 to 0.3, the transition temperature is varied by more than 50 K (i.e. from 177 to 121 K), while the RC almost maintains at a large and constant value in a certain magnetic field (i.e. about 100 J/kg at 1 T) (see Fig. 3 insert). In other word, for the investigated system, since the RC is insensitive to the Mn composition, a high performance MCE material with a high and constant RC, and a wide working temperature span over 50 K, can be achieved by mixing various La–Ce–Fe–Mn–Si compounds with different Mn compositions. This feature is of very benefit to the practical application of the $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ compounds.

4. Conclusions

The effect of Mn addition on the magnetic properties and MCE of $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ compound was investigated. It was revealed that the transition temperature is very sensitive to the Mn composition, which is shifted from 177 to 121 K for the samples with Mn composition from 0.0 to 0.3. On the other hand, with increase of Mn composition, the magnetic entropy change of the compounds is reduced, while the working temperature span is broadened. As a result, the refrigerant capacity maintains a large and constant value in a large temperature span of more than 50 K. The $La_{0.8}Ce_{0.2}Fe_{11.4-x}Mn_xSi_{1.6}$ compounds are promising magnetic entropy change materials.

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