

Crystal Structure and Magnetic Properties of $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ (R = Sm and Tb) Compounds

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This study discusses the crystal structure and magnetic properties of the rare-earth doped $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ (with R = Sm, Tb) compounds. All the samples were prepared by using arc-melting technique in argon atmosphere and the obtained result shows that after heat treatment, the samples exhibited the NaZn_{13} -type cubic phase with a small amount of a secondary α -Fe phase. The magnetic properties and magnetic entropy change were determined by mean of the temperature and field dependence magnetizations. Besides the decrease in the lattice constants, there was also observed a significant increase of Curie temperature and magnetic entropy change $-\Delta S_M$ which reached a maximum of 4.5 J/kg K for $\text{La}_{0.8}\text{Sm}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$, corresponding to a relative cooling powers (RCP) of 102 J/kg for the sample.

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1. Introduction

The search for potential materials applicable in magnetic cooling technology with large magnetocaloric effect (MCE) arrived at a class of materials with first-order phase transition. The known compounds include $\text{Gd}_5(\text{Si}_{1-x}\text{Ge}_x)_4$,¹⁾ $\text{La}(\text{Fe}_{1-x}\text{M}_x)_{13}$,²⁾ MnAs , $\text{MnFe}(\text{P}_{1-x}\text{As}_x)$,³⁾ Heusler alloys Ni-Mn-Ga ,⁴⁾ perovskite materials,⁵⁾ etc. Of those mentioned, the pseudo-binary compounds of form $\text{La}(\text{Fe}_{1-x}\text{M}_x)_{13}$ which are derived from a binary LaFe_{13} (same cubic structure as NaZn_{13}), can be stabilized by the replacement of a small amount of Fe by Si or Al. The magnetic properties of the substituted compounds depend strongly on the substituents and its concentration. For examples, the $\text{La}(\text{Fe}_x\text{Al}_{1-x})_{13}$ are all ferromagnetic within a region $0.62 \leq x \leq 0.86$ and become anti-ferromagnetic in $0.86 \leq x \leq 0.92$.²⁾ The $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ family on the other hand are ferromagnetic for $0.62 \leq x \leq 0.89$.⁶⁾ When Fe content increases, the saturation magnetization M_s also increases but the Curie temperature T_C decreases. The $\text{La}(\text{Fe}_{1-x}\text{M}_x)_{13}$ compounds usually exhibit an itinerant-electron metamagnetic transition (IEM) which associates with large magnetovolume effect, giant magnetostriction and some other properties. All of them in turn strongly influence the magnetocaloric behavior of these materials. As a result, the magnetic properties of the materials showed much stronger dependence on doping than on variation of applied magnetic field and pressure. The same was observed when substituting Co for Fe in the compound.⁷⁾ The doping of other rare earth elements such as Pr, Nd, Ce, Er and Gd into position of La were also investigated for the purpose of manipulating the Curie temperature and applied field.⁸⁻¹⁰⁾

In this report, we present some results on the effect of partial replacement of La by other rare earth elements (Sm, Tb) on the structure and magnetic properties in $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ compounds, in particular we report the data for $\text{La}_{0.8}\text{Sm}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{La}_{0.8}\text{Tb}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$.

2. Experiment

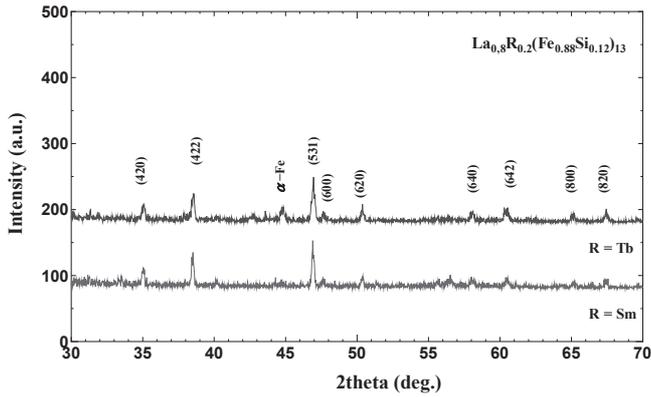
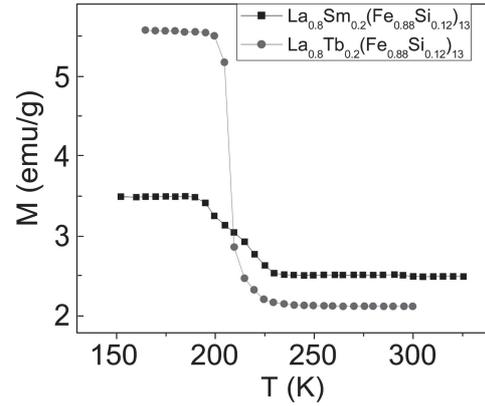
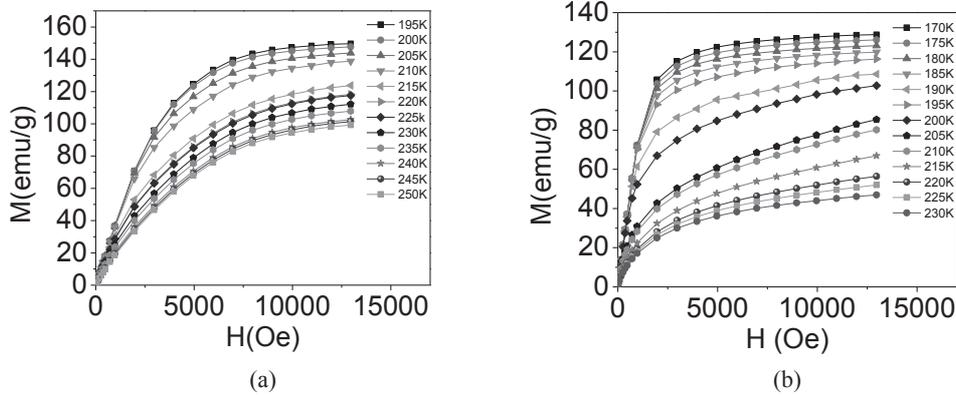
The $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ (with R = Sm and Tb) samples were prepared from the precursor materials consisting of purified metallic elements (La, Sm, Tb of 99.9%, Fe 99.99% and Si 99.999%) by using an arc-melting technique in argon atmosphere with pressure $P = 10^{-5}$ Torr. According to calculations, La and the rare-earth Sm, Tb are easy to evaporate during the melting process, therefore we supplied in surplus 2% rare-earth mass during the experiment in order to compensate the loss due to evaporation. After being melted, all samples were placed into a quartz tube, vacuumed at 10^{-5} Torr and sealed. The samples were then heated in the incubation at 1100°C for 7 days. After that, samples were immediately put in ice water. The crystal structure of samples were studied on a X-ray diffractometer Bruker D5005 (XRD) with $\text{CuK}\alpha$ radiation of wave length $\lambda = 1.54056 \text{ \AA}$ at room temperature. The magnetic properties were measured by a Vibrating Sample Magnetometer (VSM) on a DMS 880 system.

3. Results and Discussions

The X-ray power diffraction (XRD) patterns of $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ compounds (R = Sm and Tb) obtained at room temperature are showed in Fig. 1. According to these XRD, the diffraction peaks completely coincide with the peaks of a tetragonal form of the un-doped compound $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ which is derived from a cubic NaZn_{13} phase of LaFe_{13} . With substitution, a small amount of a secondary α -Fe phase was also observed.

The lattice parameters for of $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ compounds are collected in Table 1. When the lanthanum was replaced by part, we observed the decrease of the lattice parameters a , b and increase of the c axis which become longer than that of the original compound $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$.¹¹⁾ For comparison, the decrease in a , b lattice parameters is even larger than that of the Ce-doped case. This result can be explained by a smaller ionic radius of the substituted rare

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Fig. 1 X-ray diffraction patterns of $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ compounds.Fig. 2 The dependence of magnetization on temperature in $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ compounds (R = Sm and Tb) at $H = 100$ Oe.Fig. 3 The magnetization isotherms for $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ (a) R = Sm; (b) R = Tb.Table 1 Lattice parameters and Curie temperatures for the samples $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ (R = Sm, Tb).

Samples	$a = b$ (Å)	c (Å)	T_C (K)
$\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}[11]$	11.595 ± 0.004	11.594 ± 0.004	202 ± 1
R = Sm	11.455 ± 0.002	11.894 ± 0.006	215 ± 1
R = Tb	11.446 ± 0.002	11.885 ± 0.002	205 ± 1
R = Ce [12]	11.474 ± 0.002		186 ± 2

earths than that of La^{3+} (1.06 \AA). This proves that rare earth elements occurred at the La positions in the lattice.

Figure 2 shows dependence of magnetization on temperature for $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ (R = Sm, Tb) at an applied magnetic field $H = 100$ Oe. The results show that all compounds exhibit a phase transition from ferromagnetic to paramagnetic state. The T_C can be obtained directly from the derivation of these curves.

The Curie temperature T_C are listed in the Table 1. As seen, the increase in T_C in the doped samples is quite obvious, there is a 3 and 12 K increase for Tb and Sm doped samples consequently.

Figure 3 shows the magnetization isotherms for $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ measured in the external magnetic field which varies from 0 to 13.5 kOe, at selected temperatures around the T_C .

The magnetic entropy change for a particular sample can be calculated by using the following Maxwell equation:¹³⁾

$$\left(\frac{\partial S}{\partial H}\right)_{T,p} = \left(\frac{\partial M}{\partial T}\right)_{H,p} \quad (1)$$

From a collection of magnetization isotherms, the magnetic entropy change $-\Delta S$ can be obtained approximately by a relation:¹⁴⁾

$$-\Delta S = \sum_i \frac{1}{(T_{i+1} - T_i)(M_i - M_{i+1})\Delta H_i} \quad (2)$$

where M_i and M_{i+1} are the magnetization values measured at the temperature T_i and T_{i+1} in magnetic field H , respectively.

The results of the temperature dependences of magnetic entropy changes ΔS_m for the samples at a magnetic field $H = 1.3$ T are shown in Fig. 4. According to this, the $-\Delta S_m$ reaches the maximum of 3.1 and 4.5 J/kg K for Tb and Sm-doped respectively. These values are quite large if considering a relatively low applied magnetic field. Recall that, the known maximum $-\Delta S_m$ values were usually reported for $H \geq 5$ T. This value itself, however, does not reflect the cooling power of the corresponding materials, as it depends on an integral change of entropy in a whole working temperature range. Therefore, one needs to consider the relative cooling powers (RCP) - a parameter, which is defined as:¹⁵⁾

$$\text{RCP} = |-\Delta S_m|_{\text{max}} \times \delta T_{\text{FWHM}} \quad (3)$$

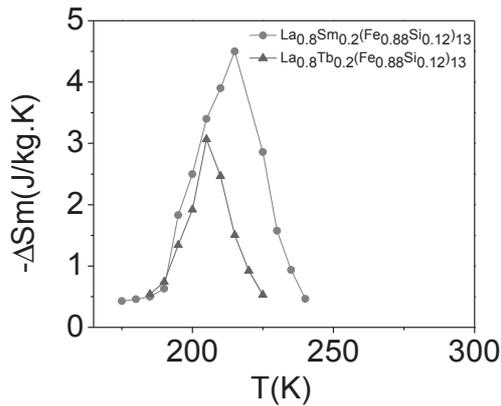


Fig. 4 The magnetic entropy change $-\Delta S_M$ for $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$.

As shown in Fig. 4, the RCP for our case is equal to 52 and 102 J/kg for $\text{La}_{0.8}\text{Tb}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{La}_{0.8}\text{Sm}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ respectively. There are several previous studies on the $\text{La}(\text{Fe}, \text{Si})_{13}$ family, which reported the higher $-\Delta S_M$ but at much higher fields. For examples, $-\Delta S_M = 5.85, 5.9$ and 3.7 (at $\Delta H = 5$ T, for $\text{LaFe}_{13-x}\text{Si}_x$, $x = 2.4, 2.6$ and 2.8 respectively);¹⁶⁾ $-\Delta S_M = 12.6$ and 9.7 J/kg K (at $\Delta H = 5$ T, for $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{La}_{0.7}\text{Nd}_{0.3}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$);⁹⁾ $-\Delta S_M = 18.67$ J/kg K (at $\Delta H = 4$ T, for 20% Ce-doped $\text{LaFe}_{11.44}\text{Si}_{1.56}$)¹²⁾... It is obvious that the values of $-\Delta S_M$ obtained from our study are nearly comparable to those of Refs. 9, 12, 16) but achieved under sufficiently lower field (1.3 T vs. 4–5 T).

4. Conclusions

The compounds $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ (R = Sm and Tb) were prepared by using an arc-melting method in argon atmosphere. After heat treatment, the compound possesses a tetragonal structure derived from a NaZn_{13} -type cubic lattice with a small amount of the secondary α -Fe phase. The lattice parameter a, b decrease but the c -axis prolongs and is longer than that of the original compound $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$. The phase transition temperature, i.e. the Curie point T_C increased with the substitution. The value of the entropy change $|\Delta S_M|_{\max}$ reached respectively 3.1 and 4.5 J/kg K and the corresponding relative cooling powers (RCP) achieved highest value of 102 J/kg for the composition

$\text{La}_{0.8}\text{Sm}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ in a low magnetic field of $\Delta H = 1.35$ T. Recall that, the high-efficient magneto-caloric materials in low magnetic field have been researched for quite long time, and this compound with its superior advantages in comparison with the other traditional refrigerating materials (such as gas-free, low cost, and high efficiency) promises direct technological application in cooling devices.

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