Magnetocaloric Effects of $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ ($\text{R} = \text{Y}, \text{Ho}$ and $\text{Yb}$) Compounds in Low Applied Magnetic Field

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Low field magneto-caloric response is important for application. We present here the results of a study on crystal structure and magnetic properties of rare-earth doped compounds $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ ($\text{R} = \text{Y, Ho and Yb}$). All samples were prepared by using arc-melting method in argon atmosphere. The lattices revealed by X-ray diffraction method show a well-defined NaZn13-type structure with small amounts of Fe phase. The dependence of magnetization on temperature $M(T)$ and on field $M(H)$ curves were recorded. The magnetic entropy change $-\Delta S_m$ and cooling powers (RCP) of compounds were estimated. The results show considerable better magnetocaloric responses of doped compounds in comparison with that of the undoped compound. [doi:10.2320/matertrans.MT-MN2019035]

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1. Introduction

In rising demands for clean gas-free refrigerating devices, the magnetic materials exhibiting large magneto-caloric effect (MCE) continuously attract the attention of scientists because of their potentials for direct application in cooling technology. The magnetic cooling devices promise high performance (above 60%), while possessing compact size and low noise.\(^1\) In order to satisfy applications the potential MCE materials have to show the following properties: (i) their Curie temperature $T_c$ should fall within specific working temperature range of considered device; (ii) the change of magnetic entropy ($-\Delta S_m$) and temperature ($\Delta T$) should be high enough in low magnetic field; (iii) lattice entropy should be low in comparison with magnetic entropy; (iv) low specific heat capacity and high thermal conductivity (reduced Foucault’s loss); and (v) high chemical stability, simple sample fabrication and low cost. Among the MCE materials, the rare earth-transition metal alloys such as $\text{LaFe}_{13},^3,^4$ Heusler alloys,$^5,^7$ perovskites,$^8$\(^9\) amorphous compounds$^{11}$ are studied for long time. There are known that each kind of materials has its own disadvantages such as high price (rare-earth compounds), low chemical stability (amorphous materials), low efficiency (perovskites) etc. Apart from the higher price, the rare-earth based $\text{LaFe}_{13}$ compounds have certain advantages, as they often possess first order phase transition near $T_c$ and their MCE are large even in low field. The available studies report on the fabrication of residual La samples,$^{14}$ ribbons-fabricated samples,$^{11}$ and on replacement of La in part by the other rare-earth elements such as Ce, Sm and Tb.$^{12,13}$ In our previous studies we show that higher values of $-\Delta S_m$ and relative cooling proficiency (RCP) could be achieved at low applied field of $\Delta H = 13.5$ kOe in Sm and Tb doped compounds.$^{12,13}$ In this work, we discuss the effects of replacing La in part by Y and the rare earth elements Ho, and Yb on structure, magnetic properties and MCE of $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ ($\text{R} = \text{Y, Ho and Yb}$) in low magnetic field of $\Delta H = 13.5$ kOe.

2. Experiment

The $\text{La}_{0.8}\text{R}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ ($\text{R} = \text{Y, Ho and Yb}$) compounds were prepared, as for the previous doped cases with Sm and Tb,$^{12,13}$ from the precursor materials consisting of purified metallic elements (La, R 99.9%; Fe 99.99%; Si 99.999%) by using arc-melting method in argon atmosphere with pressure $P = 10^{-5}$ Torr. According to calculations, to limit the effect of evaporation during melting, a surplus amount of 2% mass was added for La and doped rare-earth elements (R) to compensate possible loss. After being melted, all samples were heated by inserting into a quartz tube, vacuumed at $10^{-5}$ Torr and then sealed. The samples were incubated at 1100°C for 7 days. After removing from the incubator, the samples were immediately subjected into ice water. The crystal structure of samples were studied on X-ray diffractometer (XRD) Brucker D5005 equipped with Cu-K$_\alpha$ radiation of wavelength $\lambda = 1.54056$ Å at room temperature. Magnetic properties were measured by a Vibrating Samples Magnetometer (VSM) in temperature range from 100 to 1000 K and a magnetic field of 13.5 kOe.

3. Results and Discussion

Figure 1 shows the XRD patterns of $\text{La}_{0.8}\text{R}_{0.2}-(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ powder samples ($\text{R} = \text{Y, Sm,}^{13}$ Tb,$^{13}$ Ho and Yb) at room temperature. We redraw the diffractograms of Sm and Tb doped compounds from Ref. 13) for comparison. As seen, the diffraction peaks of all samples completely coincide with the peaks of NaZn13 structure. This means that the samples are crystallized in a cubic space group $Fm\overline{3}c$ (226). In this structure each La is surrounded in a cavity of 22 Fe atoms (Fe$_{22}$ cavity) forming a connected

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Ho (0.90), Yb (0.87). As known, the lanthanides possess from La (1.13), Y (1.03), Ce (1.02), Sm (0.96), Tb (0.92), etc., commonly referred to as the lanthanide contraction. For our purpose, the decrease of ionic radius of lanthanides as atomic number increases is due to the filling of 4f orbitals. The observed greater than expected decrease in ionic radius of lanthanides has an element of a group III (same as of La) and has the atomic number of lanthanides increases from La (57) to Y (70). The Y is an element of a group III (same of La) and has the atomic number 39. All these elements should occur in the expected oxidation state 3+ with the ionic radius (in Å) decreased from La (1.13), Y (1.03), Ce (1.02), Sm (0.96), Tb (0.92), Ho (0.90), Yb (0.87). As known, the lanthanides possess electronic configuration with increased filling of 4f states from La (4f0 5d1 6s2) to Yb (4f13 5d1 6s2). Another substituted element, i.e. Y in particular, has [Kr] electronic configuration with no 4f core (same as of La). It is evident that by removing 3 valence electrons the ionic core remains wrapped with 4f electrons and the ionic radius corresponds mainly to the size of 4f orbitals. The observed greater than expected decrease of ionic radius of lanthanides as atomic number increases is commonly referred to as the lanthanide contraction. For our cases La is replaced by sufficiently smaller ions Y, Ho and Yb, which on the other hand have more-less the same size \( \approx 0.9 \, \text{Å} \). It is interesting that the reduction of lattice constant according to the decrease of ionic radius (Fig. 1, inset) is less profound than the expected reduction calculated on the basis of linear estimation of 20% replacement of smaller ions (Table 1, 3rd col.). This may argue for the rigidity of Fe22 cavity in \( \text{Fm} \overline{3}c \) structure, and provide good evidence for the true replacements of rare-earths for La in the Fe22 cavities.

The magnetic phase transitions of doped compounds were examined by measuring the magnetization dependences on temperature. Figure 2 shows the \( M(T) \) curves obtained at low applied magnetic field of \( H = 100 \, \text{Oe} \) (the data for Sm and Tb are taken from Ref. 13). The data show that all compounds exhibit clear phase transitions from ferromagnetism to paramagnetism at Curie temperature \( T_C \) (Table 1). We have determined the \( T_C \) from these curves by linear extrapolation of inverse susceptibility according to \( T \) by Curie-Weiss law and summarize them in Table 1. As seen, the decrease of ionic radius induces the increase of \( T_C \) but \( T_C \) also shows increases upon the increased filling of 4f state (Fig. 2, insets). The exception case is the Ho-doped case where \( T_C \) drops to 198 K. This relates to the increase of ferromagnetic interaction in \( \text{LaR(Fe,Si)}_{13} \) compounds due to higher filling of 4f state of substituted element R. It is known for the lanthanides that the effective magnetic moment (in \( \mu_B \) from Landé formula \( \mu = g_J \sqrt{J(J+1)} \mu_B; \ g_J = (3/2) + [5(S+1) - L(L + 1)] / (2[J(J+1)]) \) increases from La (0) to Sm (1.7), Tb (9.8), Ho (10.7), then decreases again for Yb (4.9). These values relate to the number of unpaired electrons which increases from La (0), to Sm (5), Tb (6), and decreases for Ho (4), Yb (1). Y3+ has \([\text{Kr}]\) electronic configuration \((3d^{10}4s^24p^6)\) with 0 unpaired electron. The ferromagnetism of Ln3+ ions has both angular and orbit contributions, and this spin-orbit coupling is much larger than the ligand field splitting so the magnetism of Ln3+ ions is often independent of compounds. From Fig. 2 it is reasonable to ask about the high values of magnetization in low field and high remnant magnetization in paramagnetic region, i.e. Y (4.8), Yb (4.4), Ho (3.4), Sm (2.5) and Tb (2.2) emu/g. As seen, the compounds with elements having 0 (Y) or 1 (Yb) unpaired electron show higher magnetization values than the ones with elements having large number of unpaired electrons (Sm, Tb and Ho). This situation argues that the higher magnetization should

Table 1  Lattice parameters and Curie temperatures \( T_C \) of \( \text{La}_0.8R_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13} \) compounds. The space group is \( \text{Fm} \overline{3}c\) (226). The standard errors are given in the parenthesis.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Exp. ( a ) (Å)</th>
<th>Theor. ( a ) (Å)</th>
<th>( T_C ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La(Fe}<em>{0.8}\text{Si}</em>{0.12})_{13} ) [15]</td>
<td>11.595(4)</td>
<td>n/a</td>
<td>202(1)</td>
</tr>
<tr>
<td>( R = Y )</td>
<td>11.464(3)</td>
<td>11.390</td>
<td>207(2)</td>
</tr>
<tr>
<td>( R = \text{Sm} ) [13]</td>
<td>11.455(2)</td>
<td>11.246</td>
<td>225(1)</td>
</tr>
<tr>
<td>( R = \text{Tb} ) [13]</td>
<td>11.446(2)</td>
<td>11.164</td>
<td>219(3)</td>
</tr>
<tr>
<td>( R = \text{Ho} )</td>
<td>11.441(2)</td>
<td>11.123</td>
<td>198(4)</td>
</tr>
<tr>
<td>( R = \text{Yb} )</td>
<td>11.435(3)</td>
<td>11.061</td>
<td>229(4)</td>
</tr>
</tbody>
</table>
originate from the secondary $\alpha$-Fe phase presented in the samples (which is clearly observed for Y, and Yb (Fig. 1)). However, this phase is not seen for Ho but the Ho-compound also shows large value of magnetization, furthermore $\alpha$-Fe is seen for Tb but the Tb-compound shows quite small magnetization. It is certain that the increase of $T_C$ corresponds to the increase of ferromagnetic interactions in doped compounds but the origin of increased ferromagnetism is not clear. We leave this for future consideration, as the problem of magnetism of lanthanides is a complex problem which lies beyond the scope of this study.

Figure 3 shows the magnetization isotherms of $\text{La}_{0.8R_{0.2}}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ recorded in the variation of applied magnetic field from 0 to 13.5 kOe, as obtained for all samples in the temperature range around the particular Curie temperature. The magnetic entropy change of samples can be calculated by using the Maxwell equation:

$$\begin{align*}
\left(\frac{\partial S}{\partial H}\right)_{T, p} &= \left(\frac{\partial M}{\partial T}\right) \\
\Delta S_m &= \sum_{i} \frac{1}{T_{i+1} - T_{i}} (M_{i} - M_{i+1}) \Delta H_{i}
\end{align*}$$

From a collection of magnetization isotherms, the maximum magnetic entropy change $-\Delta S_m$ can be obtained by finding maximum of $-\Delta S$ given as follows:

$$-\Delta S = \sum_{i} \frac{1}{T_{i+1} - T_{i}} (M_{i} - M_{i+1}) \Delta H_{i}$$

where $M_i$ and $M_{i+1}$ are the magnetization values measured at temperature $T_i$ and $T_{i+1}$ in the magnetic field $H_i$, respectively. As a result, the graph of maximum magnetic entropy change $-\Delta S_m$ is a function of temperature and magnetic field (which varies from 0 to 13.5 kOe). In Fig. 4, we show that $-\Delta S_m$ of doped samples reaches the values from 3.1 to 5.8 J/kg.K.
in low magnetic field, indicating good applicability of these materials in cooling devices. The Y-doped compound appears to have the largest $-\Delta S_m$ (5.8), whereas 4.1 and 3.2 are the values for Yb and Ho-doped ones.

We calculate the relative cooling powers (RCP) based on the obtained values of magnetic entropy change $-\Delta S_m$. Here the RCP is defined as $\text{RCP} = \frac{-\Delta S_{m,\text{max}} \times 6T_{\text{FWHM}}}{T}$. The obtained RCP-s are 69, 102, 52, 28, and 90 J/kg for $R = \text{Y}$, $\text{Sm}$, $\text{Tb}$, $\text{Yb}$ and $\text{Ho}$ respectively. It is worth to note that at 13.5 kOe these values are quite large in comparison with that of other compounds available until now.

4. Conclusion

The alloy samples with composition La$_{0.8}R_{0.2}$-(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ (R = Y, Ho and Yb) are successfully prepared by means of arc-melting technique. The alloys exhibit a well defined NaZn$_{13}$ structure with lattice constant decreased upon increase of atomic number of substituted rare-earth elements. The Curie temperature $T_C$ of the compounds increases with filling of 4$f$ state, which agrees with the increased effective magnetic moment of R in the lanthanide row. The obtained MCE values range between 3.1 and 5.8 J/kg.K and the corresponding RCP-s reached highest values in low magnetic field (13.5 kOe) for Ho-doped compound (90 J/kg). The achievement of high RCP in low magnetic field is important for application of these alloys in practice. With superior advantages compared to the other MCE materials such perovskites, Heusler alloys or amorphous ribbons, the LaR(FeSi)$_{13}$ based compounds are the subjects of intensive researches widely.

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