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Structural and Magnetic Properties of LaFe$_{13-x}$Si$_x$ Nitrides

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Abstract — LaFe$_{13-x}$Si$_x$ compounds were found to have two types of crystal structure; the face-centered cubic NaZn$_{13}$-type (x $\leq$ 2.4) and the body-centered tetragonal Ce$_6$Ni$_{12}$Si$_x$-type (3.5 $\leq$ x $\leq$ 5.0). Nitrogenation has a strong effect on the cubic phase, including a large lattice expansion (6.2 to 10.8 %), an increase of Curie temperature (52 to 80 K) and spontaneous magnetization (10%). The tetragonal phase, however, was not significantly affected by the nitrogenation.

I. INTRODUCTION

Two crystal structures have been reported in transition metal-rich compounds; the cubic NaZn$_{13}$-type and the tetragonal BaCd$_{11}$-type [1]. So far the only magnetic binary alloy found with the cubic phase is LaCo$_{13}$. A single NaZn$_{13}$-type phase also exists in La(Fe$_1$-$\delta$Si$_\delta$)$_{13}$ [2],[3]. In the systems La-Ni-Si and Ce-Ni-Si, Bodak et al [4] observed that with the addition of Si up to 46 at%, a transformation from cubic to tetragonal (BaCd$_{11}$-type) structure occurs. A phase rich in Fe with tetragonal symmetry was also stabilized in PrFe$_9$Si(B)$_3$, by melt-spinning and heat treatment [1].

The intrinsic magnetic properties of many rare-earth transition-metal compounds have been found to improve dramatically with interstitial nitrogen [5], [6]. Most of the studies so far have been focused on the hexagonal and rhombohedral 2:17 and the tetragonal 1:12 compounds, although the cubic La(Fe$_{13}$-$\delta$Si$_\delta$)$_{13}$ compounds have also been investigated [7]. In this work, we prepared LaFe$_{13-x}$Si$_x$ (1.5 $\leq$ x $\leq$ 5) compounds and we have studied their structural and magnetic properties before and after nitrogenation.

II. EXPERIMENTAL METHODS

Alloys with the desired composition were prepared by arc-melting using materials with 99.9% purity. After arc-melting the alloys were vacuum annealed at 970 °C for about 4 days. The annealed alloys were pulverized to a particle size less than 45 µm. Nitrogenation was performed with N$_2$ gas in a system with a base vacuum pressure of 10$^{-5}$ torr. The system was evacuated and flushed with nitrogen gas several times to ensure a minimum oxygen content before nitrogenation. X-ray diffraction patterns of the powders were obtained using a Philips PW1710 diffractometer with a CuK$_\alpha$ radiation. The $^{57}$Fe Mössbauer spectrum was obtained by means of a constant acceleration spectrometer using a $^{57}$Co(Rh) source. The magnetic measurements were made with a SQUID magnetometer below room temperature and with a VSM above room temperature.

III. RESULTS AND DISCUSSION

A. Structures of LaFe$_{13-x}$Si$_x$ Alloys

Two crystal structures have been observed in LaFe$_{13-x}$Si$_x$ (x = 1.5 to 5.0) compounds and Fig. 1 shows their X-ray diffraction patterns. The structural parameters obtained from X-ray diffraction are listed in Table I.

For x $\leq$ 2.4, the LaFe$_{13-x}$Si$_x$ compounds were found to have a face-centered cubic (fcc) NaZn$_{13}$-type structure with the space group Fm3c. Diffraction indices were marked in Fig. 1 according to the NaZn$_{13}$-type structure. The lattice constant (a) calculated for LaFe$_{11}$Si$_2$ is 1.143 nm. There is no substantial variation of this constant with Si content.

![Fig. 1 X-ray diffraction patterns of LaFe$_{13-x}$Si$_x$ alloys.](image-url)
TABLE I
THE STRUCTURAL AND MAGNETIC PROPERTIES OF LaFe_{13-x}Si_{x} COMPOUNDS

<table>
<thead>
<tr>
<th>x</th>
<th>Struc-</th>
<th>a(nm)</th>
<th>c(nm)</th>
<th>Tc(J)</th>
<th>Ms(emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ture</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10K</td>
<td>300K</td>
</tr>
<tr>
<td>1.5</td>
<td>fcc</td>
<td>1.143</td>
<td>193</td>
<td>152.1</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>fcc</td>
<td>1.143</td>
<td>257</td>
<td>144.4</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>fcc</td>
<td>1.143</td>
<td>262</td>
<td>136.1</td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td></td>
<td></td>
<td>117.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>bct</td>
<td>0.794</td>
<td>1.164</td>
<td>103</td>
<td>71.6, 31.3</td>
</tr>
<tr>
<td>4.0</td>
<td>bct</td>
<td>0.793</td>
<td>1.166</td>
<td>88</td>
<td>61.2, 29.2</td>
</tr>
<tr>
<td>5.0</td>
<td>bct</td>
<td>0.793</td>
<td>1.169</td>
<td>82</td>
<td>18.9, 4.5</td>
</tr>
</tbody>
</table>

symmetry. The composition around x=2.8 represents a transition range from cubic to the tetragonal structure.

Between x=3.5 and 5.0, LaFe_{13-x}Si_{x} was found to have the body-centered tetragonal (bct) Ce_{9}Ni_{17}Si_{6}-type structure (space group I_{4}/mcm). The diffraction peaks were indexed accordingly. This structure is considered a distortion of the face-centered cubic Nh_{13}-type structure. The tetragonal cell is related to the cubic cell by a_{tetra} = a_{cube}/\sqrt{2}.

X-ray diffraction showed all the peaks for the tetragonal phase. In addition, a peak at about 45° was observed close to the (400) diffraction of the tetragonal phase which may also belong to Fe_{3}Si.

B. Magnetic Properties of LaFe_{13-x}Si_{x}

The Curie temperature was measured from thermomagnetic curves in an applied field of 500 Oe. The spontaneous magnetization (M_s) data were derived by extrapolating the high field (35 to 55 kOe) part of M(H) curves to zero field. The magnetic properties are summarized in Table I. Samples with the cubic structure showed a Curie temperature which was increased with increasing Si content. The spontaneous magnetization, on the contrary, decreases with increasing Si content partially because of the dilution effect of Si.

The samples with 3.5≤x≤5.0 showed two Curie temperatures (see Fig. 2 as an example), one at low temperatures and the other one above room temperature. Fig. 3 shows the Mössbauer spectrum of LaFe_{0.9}Si_{4} at room temperature. It can be seen that the spectrum consists of two sextets and a strong paramagnetic doublet. The two sextets have an area ratio 2:1, effective fields 20.0 and 21.1 T and isomer shifts (relative to Fe at room temperature) 0.26 and 0.08 mm/s, respectively. These Mössbauer parameters are typical of the Fe-Si alloy [8] which was also indicated in the X-ray diffraction analysis. The higher Curie temperature in Fig. 2 belongs to the Fe-Si alloy and the lower to the bct La-Fe-Si phase. Only the Curie temperature for the bct phase was listed in Table I. It is seen that both the Curie temperature and spontaneous magnetization decline with increasing Si contents in the bct structure.

C. Nitrogenation of LaFe_{13-x}Si_{x}

Our nitrogenation studies showed that nitrogen could enter the LaFe_{13-x}Si_{x} compounds through a gas-solid reaction. The minimum nitrogenation temperature was 650 °C, which is higher than those used for the hexagonal and rhombohedral compounds. For samples with the cubic structure, X-ray diffraction patterns (Fig. 4) on the nitrogenated samples showed that the original structures were retained and all peaks were shifted towards lower angles indicating an increase in the lattice constants. Table II lists the structural changes due to nitrogenation. The N contents were evaluated by the weight difference of the samples before and after nitrogenation. The unit cell of the cubic LaFe_{13-x}Si_{x}N_{y} expands by 6.2 to 10.8 % over the nitrogen-free parent compound. The lattice expansion led to increases in Curie temperatures by 52 to 80 K. Fig. 5 shows the thermomagnetic curves of LaFe_{13}Si_{2} before and after nitrogenation. The spontaneous magnetization was increased by 10 % with nitrogenation. Comparison of the magnetic properties of the cubic LaFe_{13-x}Si_{x} and their nitrides can be seen in Table III.

The unit cell of the tetragonal structure was also expanded by nitrogenation, but the expansion was much smaller (1.1 %

Fig. 2 Thermomagnetic data in LaFe_{0.9}Si_{4}.

Fig. 3 Mössbauer spectrum of LaFe_{0.9}Si_{4} at room temperature.

Fig. 4 X-ray diffraction patterns of LaFe_{13-x}Si_{x} before and after nitrogenation.

Fig. 5 Thermomagnetic curves of LaFe_{13}Si_{2} before and after nitrogenation.
IV CONCLUSIONS

Two types of crystal structure have been found in LaFe$_{13}$xSi$_x$ compounds; the face-centered cubic NaZn$_{13}$-type phase which occurs for $x \leq 2.4$ and the body-centered tetragonal Ce$_2$Ni$_{13}$Si$_x$-type structure for $3.5 \leq x \leq 5.0$. Nitrogenation of samples with the cubic phase expanded the unit cell by 6.2 to 10.8%. The lattice expansion led to increases in Curie temperature (52 to 80 K) and spontaneous magnetization (around 10%). Unlike the cubic phase, however, the tetragonal phase was not significantly affected by the nitrogenation.

**TABLE III**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$T_c$ (K)</th>
<th>$\Delta T_c$ (K)</th>
<th>$M_s$ (emu/g, 10K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFe$<em>{11.8}$Si$</em>{1.5}$</td>
<td>193</td>
<td></td>
<td>152.1</td>
</tr>
<tr>
<td>LaFe$<em>{11.8}$Si$</em>{1.5}$N$_{1.6}$</td>
<td>273</td>
<td>80</td>
<td>163.2</td>
</tr>
<tr>
<td>LaFe$<em>{10.8}$Si$</em>{1.6}$</td>
<td>237</td>
<td>144.4</td>
<td></td>
</tr>
<tr>
<td>LaFe$<em>{10.8}$Si$</em>{1.6}$N$_{1.2}$</td>
<td>317</td>
<td>60</td>
<td>160.0</td>
</tr>
<tr>
<td>LaFe$<em>{10.8}$Si$</em>{1.6}$N$_{1.2}$</td>
<td>262</td>
<td>136.5</td>
<td></td>
</tr>
<tr>
<td>LaFe$<em>{10.8}$Si$</em>{1.6}$N$_{1.2}$</td>
<td>314</td>
<td>52</td>
<td>145.3</td>
</tr>
</tbody>
</table>

ACKNOWLEDGMENT

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REFERENCES


