

Influence of bismuth on magnetism and magnetocaloric properties of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ intermetallic compound

A. Boutahar^{1,2,*}, K. Zehani², L. Bessais², H. Lassri¹, E.K. Hlil³

(1. LPMMAT, Hassan II University-Casablanca, Faculty of Science Ain Chock, BP 5366, Maarif- Casablanca, Morocco; 2. ICMPE-CMTR, UMR CNRS 7182, 2-8, H. Dunant St, 94320 Thiais, France; 3. Néel Institute, CNRS and Joseph Fourier University, BP 166, F-38042 Grenoble Cedex 9, France)

Received 25 September 2014; revised 8 April 2015

Abstract: Crystal structure, magnetic properties and magnetocaloric effects (MCE) of $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ ($x=0.0$ and 0.1) compounds were investigated by X-ray diffraction and magnetization measurements. The $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ compounds presented a cubic NaZn_{13} type structure. First, the magnetization behavior and the magnetic transition were analyzed in terms of Landau theory. Then, Bi substitution for La in $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ compounds led to a decrease in magnetic entropy change ($-\Delta S_M^{\text{max}}$) but an increase in Curie temperature (T_C) significantly. The significant increase of T_C by Bi substitution from 202.5 to 256 K for $x=0.0$ and $x=0.1$ respectively was attributed to an increase in the Fe-Fe exchange interactions. Moreover, magnetocaloric effect was calculated in terms of isothermal magnetic entropy change. The maximum values of ($-\Delta S_M^{\text{max}}$) of $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ for $x=0.0$ and 0.1 compounds were found to be, respectively, 22.56 and 4.36 J/(kg·K) under an applied magnetic field change of 5 T. For the same applied magnetic field ($\mu_0 H=5$ T), the relative cooling power (RCP) values were found to vary between 487 and 296 J/kg.

Keywords: NaZn_{13} ; itinerant-electron metamagnetic transition; magnetocaloric effects; rare earths

Solid-state materials with the magnetocaloric effect are considered to be very promising in creation of solid-state refrigerators with high efficiency and ecological compatibility^[1-4].

Among magnetocaloric materials, $\text{La}(\text{Fe},\text{Si})_{13}$ based compounds are currently the most promising. However, LaFe_{13} is not stable because of its positive formation enthalpy. To obtain a LaFe_{13} based alloy, a third element has to be introduced. A stable $\text{LaFe}_{13-x}\text{M}_x$ compound was obtained by Kripyakevich et al.^[5] after partially replacing Fe with Si or Al.

$\text{LaFe}_{13-x}\text{Si}_x$ compounds ($x \leq 1.6$) of the NaZn_{13} type structure^[6,7] exhibit a large magnetic entropy change in the vicinity of Curie temperature T_C ^[8] and it is typical for relatively low cost materials with a high potential as operational magnetic refrigerants around room temperature. The large entropy changes in $\text{LaFe}_{13-x}\text{Si}_x$ compounds are associated with the negative lattice expansion around T_C and the first-order field-induced ferromagnetic (FM) to paramagnetic (PM) itinerant-electron transition above T_C ^[9]. Given that, the Curie temperature of $\text{LaFe}_{13-x}\text{Si}_x$ is usually lower than 210 K, significant efforts have been made in order to enhance T_C and retain the large MCE performance. Among the approaches taken are: (1) introduction of interstitial atoms (hydrogen or carbon)^[10,11]; (2) elemental substitution (substituting La ^[12] and Fe ^[13] by another rare-

earth or transition metal); (3) modification of synthesis methods (arc melting or induction-melting with various heat treatments^[14], melt spinning^[15] and ball milling^[16]).

In this paper, we reported on the influence of Bi substitution for La in $\text{LaFe}_{11.4}\text{Si}_{1.6}$ compound on the structural, magnetic behavior, magnetic phase transition and magnetocaloric properties.

1 Experimental

The compounds with nominal composition $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ ($x=0.0$ and 0.1) were prepared by mechanical alloying. A mixture of high-purity powders of La, Bi, Fe, Si and pre-alloyed LaBi and LaSi were milled in steel vials hermetically sealed in an argon filled glove box with O_2 and H_2O rate of 1 ppm. The high energy ball milling process was performed in a Fritsch planetary ball mill (Pulverisette P7) with five steel balls of 15 mm for 5 h^[17,18]. The rotational speed of the vial and the disk were 1500 and 600 r/min respectively. The powders were subsequently heat treated for 30 min at a temperature equal to 1473 K in evacuated quartz tubes and quenched in water.

The structure was studied by means of a Bruker D8 X-ray diffractometer with automatic divergence slit (Cu $K\alpha$ radiation $\lambda=0.154178$ nm). The refinement of X-ray diffraction (XRD) patterns was carried out using the

* Corresponding author: A. Boutahar (E-mail: boutahar.fsac@gmail.com; Tel.: +212522230680)

FullProf code based on the Rietveld technique. The Rietveld method was used to analyze the crystal structures and to calculate the lattice parameters, the diffraction domain size and strain rate. The weight percentage of each of the coexisting phases was directly obtained with the approximation of a Brindley absorption factor equal to 1. Isotropic Lorentzian and Gaussian contribution of size and micro-strains were taken into account. The “goodness of fit” indicator R_B was calculated as in Refs. [19–21].

The magnetization was measured using Physical Properties Measurement System PPMS9T Quantum design equipment and a maximum applied field of 9 T on sample in epoxy resin.

2 Results and discussion

Fig. 1 displays the XRD patterns and Rietveld refinement for $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ compounds with $x=0.0$ and 0.1. The Rietveld refinement confirms that, the sample with $x=0.0$ crystallized in a single phase of the cubic NaZn_{13} type structure (space group: $Fm\bar{3}c$). However, a small amount of the $\alpha\text{-Fe}$ (<10%) and La_2O_3 (<5%) phases is found in the sample with $x=0.1$.

In these compounds, the La, 8a, the Bi, 8a and Fe₁, 8b sites are fixed at (1/4, 1/4, 1/4), (1/4, 1/4, 1/4) and (0, 0, 0), respectively. The fractional coordinates for the Fe₂, 96i sites are (0; y; z). The lattice parameter a , the atomic positions, R_B and χ^2 factors, obtained from the best

refinement are given in Table 1.

From the lattice parameter and the atomic positions, the interatomic distances were calculated. The latter does not change too much with the composition. In agreement with previous works^[22,23], the refinements show that Si atoms preferentially order in the higher multiplicity site (96i) which are the nearest neighbors of La atoms.

The enthalpy of mixing for La-Fe is positive, which means no formation of binary La-Fe phase^[24]. The introduction of Bi into $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ starts to produce large differences in affinity between the La-Si and the La-Fe pairs, gradually changing the interatomic distances of the pairs, while the structural stability of clusters (domain of NaZn_{13} structure) will be lowered.

The XRD results show that the lattice parameter of the $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ alloys decreases with Bi content from 1.14742 to 1.14679 nm for $x=0.0$ and 0.1 respectively since the atomic radius of Bi (0.17 nm) is lower than that of La (0.187 nm). However, this increase is also a good indication of the insertion of Bi atoms into the La-Fe phase. Both the compounds with $x=0.0$ and 0.1 are ferromagnetic. Fig. 2(a) shows the magnetization $M(T)$ of the samples as a function of temperature in a field of 10 mT.

The Curie temperatures were determined from maximum change of the $dM/dT(T)$ curves (Fig. 2(b)). One can see that the Curie temperature increases with increasing Bi concentration. It passes from 202.5 K in the case of $x=0.0$ to 256 K for $x=0.1$. The significant increase of T_C by Bi substitution could not only be attributed to the magnetovolume effect ($\Delta V/V=0.13\%$), but also probably be due to the Fe-Fe exchange interactions. Indeed, the PowderCell software was used to compute the La(8a)-Fe(96i), Fe(8b)-Fe(96i) and Fe(96i)-Fe(96i) bond lengths to explain the increase in T_C . Table 2 shows the interatomic distances with Bi content for $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ ($x=0.0$ and $x=0.1$) compounds.

Thus, the observed enhancement of T_C can be attributed to an increase in the Fe-Fe exchange interactions caused by the decreasing Fe-Fe distances, which can be reproduced by using the Bethe-Slater curve. A similar increase of T_C was observed with x for $\text{La}_{1-x}\text{Nd}_x\text{Fe}_{11.44}\text{Si}_{1.56}$ and $\text{La}_{1-x}\text{Er}_x\text{Fe}_{11.44}\text{Si}_{1.56}$ compounds, respectively^[25,26].

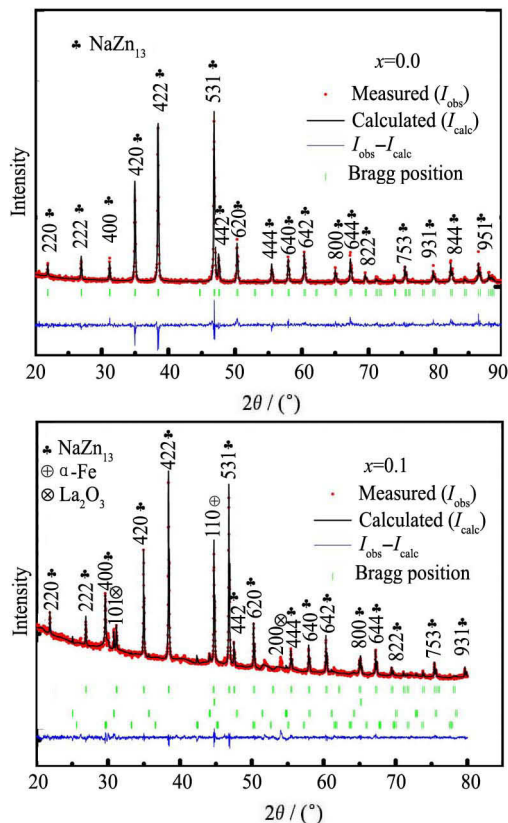


Fig. 1 XRD patterns of $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ ($x=0.0$ and 0.1) compounds by use of the Rietveld method

Table 1 Crystallographic parameters from a Rietveld refinement of $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ annealed at 1273 K*

	$x=0.0$	$x=0.1$
a/nm	1.14742 (2)	1.14694 (2)
V/nm^3	1.511	1.509
$y(96i)$	0.1192(2)	0.1170(1)
$z(96i)$	0.1806(2)	0.1798(1)
χ^2	1.30	1.53
R_B	3.42	2.54

* a is unit cell parameter, V is unit cell volume, χ^2 and R_B are agreement factors

Download English Version:

<https://daneshyari.com/en/article/1261713>

Download Persian Version:

<https://daneshyari.com/article/1261713>

[Daneshyari.com](https://daneshyari.com)