Chapter 10

Effect on Heat Treatment and Doping of Cubic $NaZn_{13}$-Type $La_{0.7}Pr_{0.3}(Fe,Si)_{13}$ for Magnetic Refrigerator Application

Muhamad Faiz Md Din, Jianli Wang and

Mohd Taufiq Ishak

Additional information is available at the end of the chapter

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Abstract

Soft ferromagnetic cubic $NaZn_{13}$-type $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ has turned out to be a standout amongst the most fascinating compounds for investigating substantial magnetocaloric effect (MCE) on the grounds that the attractive properties of this compound shows large enough spontaneous magnetization for applications, strongly doping dependent, and as well as delicate soft ferromagnetism. These impacts can be attributed to the itinerant electron metamagnetic (IEM) transition especially around the first-order magnetic transition region. However, this compound is difficult to frame by the basic cementing process because of the inherent deficiency of the peritectic response, γ-Fe + La → $La(Fe,Si)_{13}(\tau_{1a})$, which frequently brings about a blended microstructure of α-Fe + $La(Fe,Si)_{13}(\tau_{1a})$ + $LaFeSi(\tau_4)$. Additionally, dependability of $La(Fe_xSi_{1-x})_{13}$ is no middle-of-the-road stage and common solvency amongst Fe and La in the Fe-La framework as a reality is represented by response dispersion as indicated by magnetic and electronic states' contribution. From this point of view, the structure, attractive properties and MCE of this compound have been talked about in detail as indicated by various temperatures and times of the annealing treatment. In addition, efficiently contemplating on the doping impact from various concentrations of transition metal elements such as Copper (Cu) and Chromium (Cr) on Iron (Fe) in the $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ compound is likewise discussed.

Keywords: intermetallic, structure properties, magnetocaloric effect, magnetic properties, magnetic application

1. Introduction

Attractive refrigeration moves toward becoming more solid to supplant the ordinary refrigeration frame work due to its favourable circumstances utilizing magnetocaloric effect (MCE) application. This innovation has brought huge points of interest as high refrigeration efficiency, environment friendly, practical of volume size, cheapest, nondangerous, and out of sound pollution draw in to additionally look into, contrasted/compared to conventional gas pressure refrigeration system. The MCE was initially found by Warburg [1] in 1881, and since the discovery of the giant magnetocaloric effect at room temperature in 1997 [2], attractive materials with expansive MCE have been widely examined tentatively and hypothetically in the previous two decades. Up to the present time, various materials with impressive magnetic

Nominal composition	Condition of case study	Ref
$La(Fe_{13-x}Si_x)$ Different of Si concentration	Tc found to increase from 195 K for Si=1, 195 K for Si=1.2, 210 K for Si=1.43, 222 K for Si=1.6 and 231 K for Si=1.8	[7]
$La(Fe_xSi_{1-x})_{13}$ Different of Fe concentration	Tc found to decrease from 208 K for Fe=11.4, 195 K for Fe=11.44, 188 K for Fe=11.57 and 184 K for x=11.7	[9]
$LaFe_{11.4}Si_{1.6}$	Tc=209 K	[10]
$LaFe_{10.98}Co_{0.22}Si_{1.8}$	Tc=242 K	
$LaFe_{11.13}Co_{0.71}Al_{1.17}$	Tc=279 K	
$La_{0.7}Pr_{0.3}(Fe_{13-x}Si_x)$ Different of Si concentration	Tc found to increase from 168 to 218 K for Si=1.5 to Si=2.0	[11]
$LaFe_{10.6}Si_{2.4}$	Tc=242 K	[12]
$LaFe_{11.44}Co_{0.13}Si_{1.43}$	Tc=205 K	[13]
$LaFe_{11.44}Co_{0.39}Si_{1.17}$	Tc=240 K	
$LaFe_{11.44}Co_{0.52}Si_{1.04}$	Tc=250 K	
$LaFe_{11.4}Si_{1.6}$	Tc=200 K	[14]
$La_{0.9}Er_{0.1}Fe_{11.4}Si_{1.6}$	Tc=205 K	
$La_{0.7}Er_{0.3}Fe_{11.4}Si_{1.6}$	Tc=214 K	
$LaFe_{11.4}Si_{1.6}$	Large MCE with reversible magnetic phase transition at Tc	[8]
$La_{1-x}R_xFe_{11.5}Si_{1.5}$ R=Ce, Pr, Nd	Tc found to increase up to 11% when 30% of La replaced by R element	[15]
$La(Fe_xSi_{1-x})_{13}H_y$ Doping of Hydrogen y= 0, 0.5, 1.0 and 1.5	Tc found to increase from 195 to 330 K for y=0 to 1.5	[19]
$La_{0.7}Pr_{0.3}Fe_{11.4-x}Cu_xSi_{1.6}$ Different of Cu concentration	Tc found to increase from 197 K for x=0, 210 K for x=0.06, 218 K for x=0.12, 224 K for x=0.23 and 230 K for x=0.34	[25]
$La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ Different of Cr concentration	Tc found to decrease from 197 K for x=0 to 180 K for x=0.06 and start to increase till 185 K for x=0.12, 190 K for x=0.23 and 195 K for x=0.34	[26]

Table 1. Brief summary of previous study related to $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ compound.

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entropy change values have been observed, for example, $Gd_5Si_2Ge_2$ [2], $NdMn_{2-x}T_xSi_2$ (T = transition metal = Cr, Cu, V, Ti) [3–5], $MnAs_{1-x}Sb_x$ [6] and $La(Fe,Si)_{13}$ [7–9].

The cubic $NaZn_{13}$-type $La(Fe,Si)_{13}$ winds up noticeably as one of the intriguing compounds to investigate large MCE because of their attractive properties, for example, firmly doping reliant, sufficiently extensive unconstrained charge and delicate soft ferromagnetism [10–12]. These impacts can be attributed to the itinerant electron metamagnetic (IEM) change in the region of the primary request progress temperature. Doping other attractive rare earth elements, for example, Pr, Nd, Ce, Er and Gd, substitute the La position which was utilized to change the temperature and diminish the critical field of 3*d*-metamagnetic progress in $La(Fe,Si)_{13}$ compound [13–15] in light of the fact that the rare earth-Fe magnetic coupling in this system shows a solid reliance on the kind of the rare earth element, respectively.

The cubic $NaZn_{13}$ type is difficult to be formed by regular solidification process because of the characteristic inadequacy of a peritectic response, $\gamma\text{-Fe} + L \rightarrow La(Fe,Si)_{13}(\tau_{1a})$, which frequently results in the blended microstructure of α-Fe + $La(Fe,Si)_{13}(\tau_{1a})$ + $LaFeSi(_{\tau 4})$ [16]. Many researchers set up this compound treatment in the range of 1173–1323 K for at least 10 days to produce the $NaZn_{13}$-type structure [17–19]. However, the peritectic response temperature in $La(Fe,Si)_{13}$ is around 1673 K regarding the La-Fe quasi table diagram [20] and the temperature was found to be more beneficial in the shorting-stage change process [21] as demonstrated by Liu et al. [22] and Chen et al. [23]. Both these groups revealed that the readiness in temperature range around 1323–1623 K can create most measures of the $NaZn_{13}$-type structure. **Table 1** indicated the variable case study related to the $NaZn_{13}$ type which showed different physical properties' behaviour in substitution or doping effect on the $La(FeSi)_{13}$ compound, respectively.

According to Shen et al. [24] findings, substituting La with other rare earth component can prompt surprising improvements of magnetic entropy change. However, these behaviors come with an expansion hysteresis loss as the nature of first-order magnetic transition. In this chapter, we clarify in detail the impact of different temperature-annealing processes on the structure and magnetic properties of $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$. The influence of Cu and Cr doping with the substitute of Fe in the $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ compound on magnetic properties and magnetocaloric effect was also explained.

2. The phase relation between low temperature with long-time annealing (LTA) and high temperature with short-time annealing (HTA)

2.1. Structural properties

It was all around acknowledged that the stage level of impurity structure in the $NaZn_{13}$-type compound is dependent on the procedure of preparation process [25, 26]. Starting there, the $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ compound was chosen to be set up with two different annealing treatments with low-temperature annealing (LTA) at 1323 K for 14 days and high-temperature annealing (HTA) at 1523 K for 4 h to elucidate which method is more advantageous and forms a better

$NaZn_{13}$-type structure. Results from XRD diffraction (as indicated in **Figure 1**) show that the HTA with less time can form a bigger number of the NaZn13– compound structure phase compared to LTA with long-time annealing process. LTA produces substantially an amount of impurity, LaFeSi and α-Fe phase in the $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ compound.

It is shown in **Table 2** that the LTA procedure brings about less amount of the $NaZn_{13}$ structure though the peritectic reaction alludes to refined structure. This behaviour happens with respect to non-equilibrium solidification phenomenon regarding the uncompleted peritectic response γ-Fe + L → $La(Fe,Si)_{13}(\tau_{1a})$ [16]. At the point when the annealing temperature is higher, the speed of the dispersion of atom is just large during the high temperature and solid-phase diffusion reaction process. Along these lines, it unmistakably happens that while expanding the annealing temperature to 1523 K for 4 h (HTA), the measure of the $NaZn_{13}$ structure steadily formed will eliminate nearly all of the LaFeSi structure and decrease the amount of the α-Fe structure. The Retiveld refinement is indicated in **Table 2** and it is shown that the weight of $NaZn_{13}$ structure increases from 69% at LTA to 96% while the weight amount of LaFeSi and the α-Fe stage at HTA is found to decrease. The constitutions of the formed $NaZn_{13}$ structure in 1523 K for 4 h of annealing treatment are in concurrence with other groups [22, 23]. However, it was hard to shape a single-structure sample by the bulk synthesis technique as a low cooling rate of the solidification procedure which will deliver an inhomogeneous structure to the sample. That is the reason, with a specific method in order to stay away from recrystallization of α-Fe and the LaFeSi structure, the samples were quickly quenched in water.

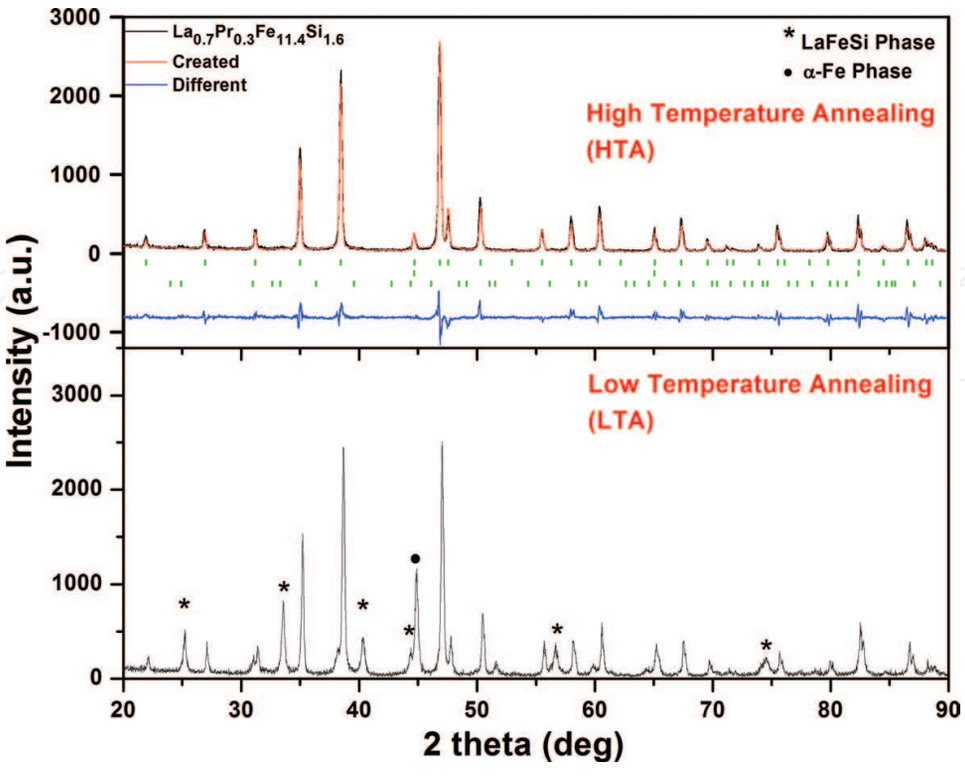

Figure 1. Room temperature X-ray diffraction patterns of $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ produced by the HTA and LTA processes.

Nominal composition	Heat treatment (T(K)/t)	Phase	Wt%	Refined composition	Lattice parameter, a (Å)
$La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$	1323 K/14 days	$Nazn_{13}$	69.05	$La_{0.7}Pr_{0.3}Fe_{14.1}Si_{2.1}$	11.45104
	(LTA)	α-Fe	19.42		2.86435
		LaFeSi	11.53		
$La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$	1523 K/4 hours	$Nazn_{13}$	96.12	$La_{0.7}Pr_{0.3}Fe_{11.00}Si_{1.6}$	11.45845
	(HTA)	α-Fe	3.56		2.86563
		LaFeSi	0.32		

Table 2. Synthesis conditions (heat treatment process) and results of the structural characterization (phase observed, analyzed compositions, and lattice parameter of the $NaZn_{13}$, α-Fe, and LaFeSi phases) for LTA and HTA from XRD.

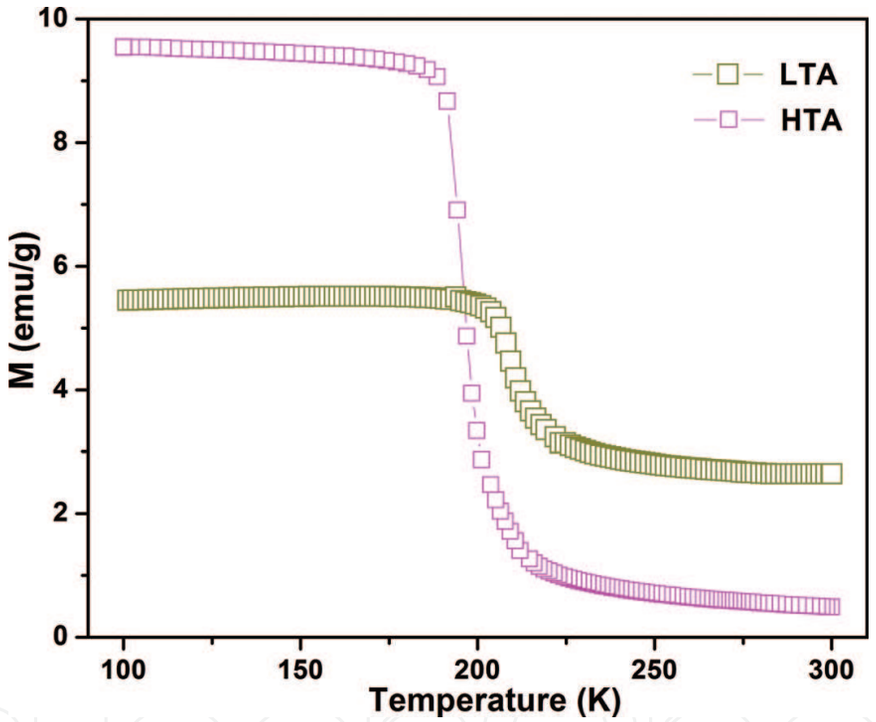

Figure 2. Temperature dependence of magnetization of $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ for LTA and HTA.

2.2. Magnetic properties

Figure 2 demonstrates the temperature dependent of magnetization measured under the low magnetic field of 0.01 T in temperature range from 100 to 300 K of the $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ compound for LTA and HTA. The TC values were characterized as a maximum of dM/dT from **Figure 2**. It found that TC of the $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ compound from LTA treatment is ~ 200 K which is 13 K higher than HTA treatment as ~197 K. Furthermore, LTA has different magnetic phase transition characteristics because of the different Si concentration in the $NaZn_{13}$ phase compared to HTA, in which LTA is formed with higher Si concentration and contributes to expand TC and changes the magnetic state from first-order to second-order transition in this case study. Moreover, LTA treatment also interfaced to produce more impurity such as α-Fe and

LaFeSi structure and decrease the main $NaZn_{13}$ structure content with respect to temperature and time during annealing process, which troubles in solution treatment at low temperature directly increasing the Si concentration behaviour. In **Table 2**, it is shown from XRD refinement that the concentration of Si in the $NaZn_{13}$ structure for LTA is higher compared to HTA. As far as the impacts of expanding the Si concentration in the $NaZn_{13}$ structure is concerned, we suggest that this marvel adds to expanding the value of T_C and changes the magnetic phase transition. Comparative phenomena likewise have been reported by Bo Liu et al. [27].

Magnetic hysteresis loss (as shown by the territory encased between ascending and descending branches of the magnetization curves) is additionally normal for first-order magnetic transition. The magnetization curves obtained for $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ (LTA and HTA) for fields in the range B = 0–5 T around their ferromagnetic ordering temperatures have been studied respectively [25]. This information was obtained for increasing and decreasing fields at 5 K and 2 K intervals at 200 K around T_C, consequently giving data about magnetic hysteresis loss effect as discussed using the below Equation [28].

$$\text{Magnetic hysteresis loss} = \int_{\text{decrease } H}^{\text{increase } H} (\partial M)_H \, dH \tag{1}$$

As exhibited in **Figure 3**, examination of the magnetic hysteresis loss around the ferromagnetic ordering temperatures for $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ (LTA and HTA) is up to ~ 12.4 J kg^{-1} (demonstrated value for B = 0–5 T as appropriate to compare) for $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ (HTA) at T_C ~ 197 K, while almost no magnetic hysteresis loss of ~ 0.1 J kg^{-1} is found for $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ (LTA) around T_C ~ 210 K. It is exhibited that the field which actuated the first-order magnetic transition from paramagnetic to ferromagnetic was eminently debilitated by the more Si concentration in LTA which demonstrated second-order magnetic transition as a contrast with HTA which showed

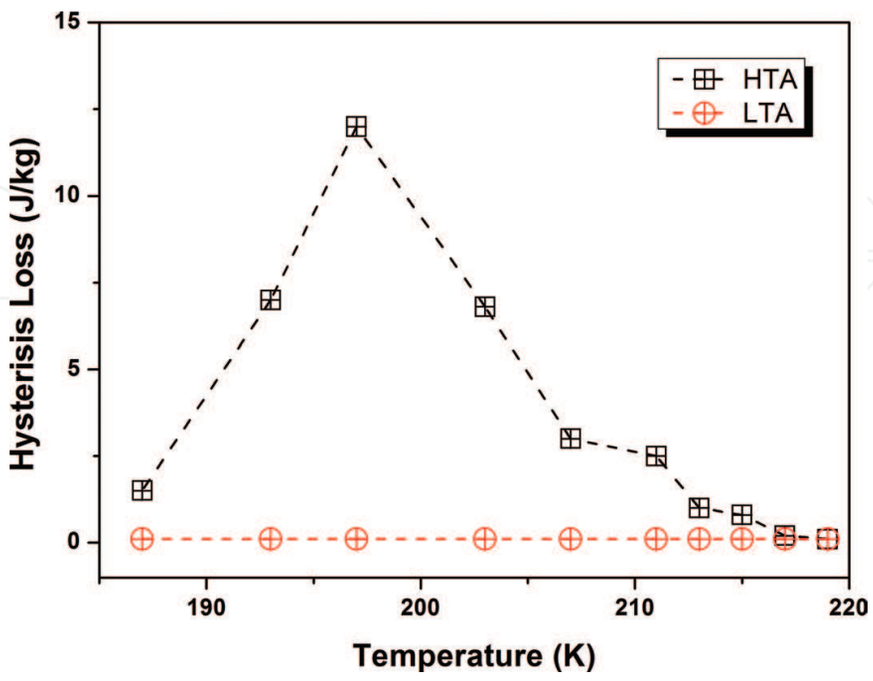

Figure 3. Comparison of the magnetic hysteresis losses for $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ produced by the HTA and LTA process under magnetic fields over the ranges *B* = 0–5 T.

first-order magnetic transition. The upside of the sample without hysteresis loss expands the proficiency of magnetic refrigerator application [29] which is of little vitality loss during temperature change in the cycle operation system.

2.3. Magnetocaloric effect

Giant MCE value and magnetic entropy changes are generally accompanied with a first-order magnetic transition because of an extensive rate of change in magnetic field. Even these materials have been preferred in terms of the MCE value compared to second-order material; the issues of thermal and magnetic hysteresis loss are impossible to solve. So as to fulfill the reasonableness of various tests and related logical ways to deal with, calculation of the isothermal entropy change, $-\Delta S_M$, in this study, has been characterized from the decreased field of magnetization measurement by the Maxwell relation [30, 31]:

$$-\Delta S_M(T, H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \tag{2}$$

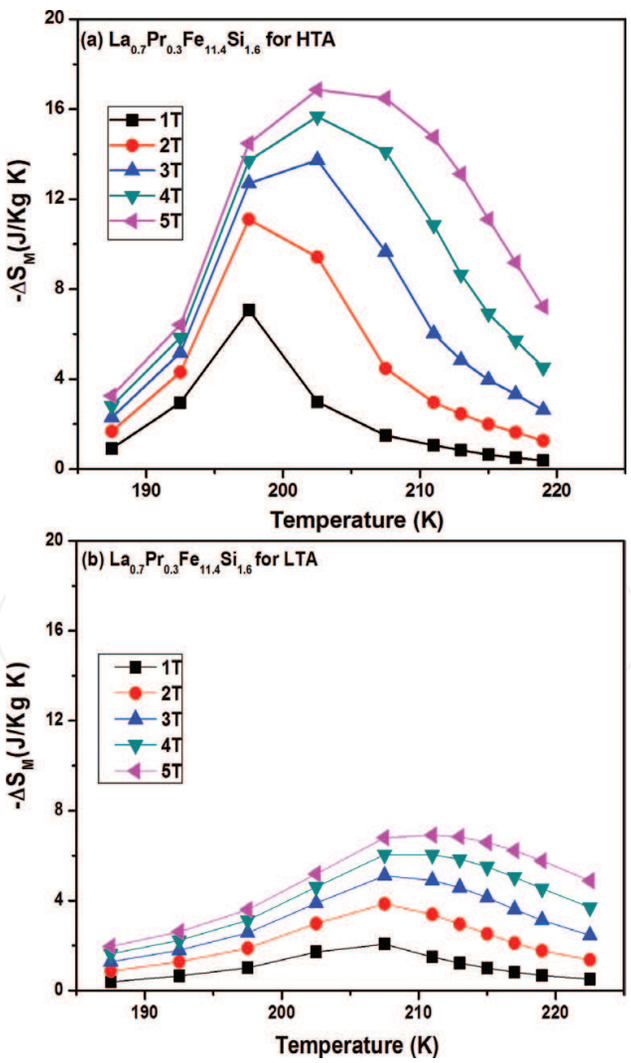

Figure 4. Magnetic entropy change, $-\Delta S_m$, for a 0–5 T change in field of $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ for (a) HTA and (b) LTA compounds as a function of temperature.

The $-\Delta S_M$ peak gradually broadens toward higher temperatures with increasing magnetic field (from ΔB = 0–5 T) as shown in **Figure 4(a)** and **(b)** for $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ (LTA and HTA) related to behaviour of a field-induced transition from the paramagnetic to ferromagnetic state, respectively. The changes in magnetic entropy for $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ (LTA and HTA) around their ferromagnetic ordering temperatures as indicated in **Figure 4** are calculated from decreasing applied fields in order to satisfy the isothermal entropy change and suitability of different experiments [32]. The MCE values are $-\Delta S_M \sim 16.8$ J kg^{-1} K^{-1} at T_C = 197 for HTA and decrease to $-\Delta S_M \sim 7.9$ J kg^{-1} K^{-1} at T_C = 200 K for LTA. The decrease in the value of $-\Delta S_M$ is related to increase in Si and there is less magnetization moment concentration in $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ (LTA) compared to $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ (HTA). This phenomenon indicated that $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ (HTA) is more favorable and advantageous compare to $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ (LTA) as a refrigerant in the magnetic refrigerator application.

3. The influence of phase and properties in $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ with partial substitution of Cu for Fe

3.1. Structural properties

$La_{0.7}Pr_{0.3}Fe_{11.4-x}Cu_xSi_{1.6}$ (x = 0–0.34) is prepared using the HTA method. As indicated in **Table 3**, the amount of α-Fe and LaFeSi phases increases with Cu-doping contribution. This behaviour occurs when we substitute Cu for Fe in $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ and it affected the bulk diffusion rate controlling factor of homogenization in the $NaZn_{13}$–type structure. **Table 3** shows the LaFeSi and α-Fe phase fractions in $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cu_xSi_{1.6}$ which increases with the increasing Cu substitution while the $NaZn_{13}$ phase decreases from 96% at x = 0 to 85% at x = 0.34. In the La-Fe-Si ternary system, the substitution new element directly influences the La-Si and Fe-Si bonding as discussed in detail from the previous study [27]. The substitution of Cu into Fe in $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ produces the differences in relation between the La-Si and La-Fe pairs, changing the interatomic distances which contribute to affecting the structural stability of the $NaZn_{13}$ structure. As discussed by Fujita et al. [19], that diffusion, also sensitive to modification of both the electronic structure and lattice spacing, then agrees well with this study which takes in different atomic radii of Cu (1.28 Å) and Fe (1.24 Å).

3.2. Magnetic properties

As indicated in **Table 3**, increase in Cu doping in $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ will increase the T_C and change the magnetic phase transition from first- to second-order type. This behaviour found that related exchange interactions exist between Fe-Fe in the Fe-rich rare earth intermetallic compounds. It is related to the phenomenon when the separation of the Fe–Fe pair is smaller than 2.45 Å, the exchange interaction will be negative but the interaction is positive at larger Fe–Fe distances as similarly reported by other group [31]. Based on the fact that the atomic radius of Fe is smaller than that of Cu, increase in Cu concentration doping will increase the lattice parameter and the Fe-Fe distance then will enhance the positive interactions with increasing T_C.

Nominal composition $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cu_xSi_{1.6}$	**X = 0**	**x = 0.06**	**x = 0.12**	**x = 0.23**	**x = 0.34**
Phase (Wt%)	Nazn13 (96.12%)	Nazn13 (91.68%)	Nazn13 (88.20%)	Nazn13 (86.83%)	Nazn13 (85.20%)
	α-Fe (3.56%)	α-Fe (7.33%)	α-Fe (9.06%)	α-Fe (10.15%)	α-Fe (10.63%)
	LaFeSi (0.32%)	LaFeSi (0.99%)	LaFeSi (2.74%)	LaFeSi (3.02%)	LaFeSi (4.16%)
Lattice parameter, a (Å)	11.45845	11.46035	11.46274	11.46495	11.46621
Tc (K)	197	210	218	224	230
$-\Delta S_M$ (J/kg K)	17	12	9	7	5
RCP (J/Kg)	400	330	300	280	245
MS (μB/ f.u.) at 5 K	22.8	22	21.6	21	21.4

Table 3. Results of the structural characterization (phase observed, analyzed compositions, and lattice parameter of the $NaZn_{13}$, α-Fe, and LaFeSi phases) magnetic and magnetic entropy change for $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cu_xSi_{1.6}$ (x = 0, 0.06, 0.12, 0.23, 0.34) [25].

As details included in **Table 3**, the compounds were found to exhibit ferromagnetic behaviour with a saturation magnetization below 24 μ_B/f.u. [25]. However, it is shown that the replacement Cu for Fe will reduce the saturation magnetization field in $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cu_xSi_{1.6}$ according to the characteristics of Cu as a diamagnetic element. As we assume no contribution from the Pr moment with increasing Cu content, the average moment of the Fe can be derived from the total moment. It is indicated that substituting Fe by Cu leads to a decrease in the average moment of the Fe in $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$. This agrees well with x = 0.34; the value of the saturation magnetization is higher than expected. The saturation magnetization is higher because the total moment is included with a large amount of the α-Fe moment in $La_{0.7}Pr_{0.3}Fe_{11.06}Cu_{.34}Si_{1.6}$.

3.3. Magnetocaloric effect

The values of $-\Delta S_M$ around T_C that have been derived from the decrease in magnetic field are shown in **Table 3** as a function of temperature with a 0–5 T change in the field for $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cu_xSi_{1.6}$ (x = 0–0.34) compounds. It is shown that the $-\Delta S_M$ peak gradually becomes broader at higher temperatures with increasing magnetic field from 1 to 5 T as characteristic of the field-induced IEM transition from the paramagnetic to the ferromagnetic state particularly around temperatures above T_C. Furthermore when there is increase in the concentration of Cu in $La_{0.7}Pr_{0.3}Fe_{11.4-}Si_{1.6}$, the $-\Delta S_M$ decreases from 17 J/kgK for x = 0 to 5 J/kgK for x = 0.34 as it is proved that Cu is dilute and not a magnetic element.

The relative cooling power (RCP) is very important and related to the magnetic refrigerator application performance. Using the full width at half maximum of the peak in the temperature dependence of the magnetic entropy change $-\Delta S_M$ and the maximum of the entropy variation $-\Delta S_M^{max}$, the value of RCP has been calculated using the following formula [19, 33]:

$$RCP = -\Delta S_M^{max} \delta T^{FWHM} \quad (3)$$

A summary of RCP values and other magnetic characterization parameters listed in **Table 3** for $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cu_xSi_{1.6}$ (x = 0, 0.06, 0.12, 0.23, 0.34) compounds is presented. The RCP value shows the similar behaviour with MCE which starts to decrease from 400 J/kg for x = 0 to 245 J/kg for x = 0.34 on application of a B = 0–5 T, respectively.

4. The influence of phase and properties in $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ with partial substitution of Cr for Fe

4.1. Structural properties

The x-ray diffraction analysis at room temperature in **Table 4** showed that Cr concentration contributes to an increase in the amount of α-Fe and LaFeSi phases from the beginning to x = 0.06. However it was found to increase from x = 0.12 to x = 0.34. We suggest this behaviour to be related to bulk diffusion rate controlling factor of homogenization in the cubic $NaZn_{13}$–type phase structure (space group *Fm3c*) by substitution of Cr for Fe. **Table 4**, shows that the weight fraction of the $NaZn_{13}$ structure decreases from 96% at x = 0 to 85% at x = 0.06 and then increases to 97% with increasing Cr content till x = 0.34. The replacement of Cr for Fe into $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ starts to produce large differences between the La-Si and the La-Fe pairs which effect to decrease the stability on clusters of the $NaZn_{13}$ phase. That diffusion is also sensitive to modification of both the electronic structure and lattice spacing [34] agrees with the phenomenon of lattice parameter *a*, which decreases from 11.458 Å at x = 0 to 11.451 Å at x = 0.34; even Cr atomic radius is larger than Fe and at different electronic environments (Fe ~ $3d^64s^2$ and Cr ~ $3d^54s^1$, respectively).

4.2. Magnetic properties

The temperature dependence of the magnetization for calculated T_C of $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ compound is measured under magnetic field of 0.01 T as shown in **Table 4**. T_C was found to

Nominal composition $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$	**X = 0**	**x = 0.06**	**x = 0.12**	**x = 0.23**	**x = 0.34**
Phase (Wt%)	Nazn13 (96.12%)	Nazn13 (85.90%)	Nazn13 (92.60%)	Nazn13 (94.00%)	Nazn13 (97.60%)
	α-Fe (3.56%)	α-Fe (10.6%)	α-Fe (6.00%)	α-Fe (4.70%)	α-Fe (2.30%)
	LaFeSi (0.32%)	LaFeSi (3.55%)	LaFeSi (1.40%)	LaFeSi (1.30%)	LaFeSi (0.20%)
Lattice parameter, a (Å)	11.45845	11.45560	11.4540	11.45240	11.45180
Tc (K)	197	180	185	190	195
$-\Delta S_M$ (J/kg K)	17	12	14.2	15.6	17.5
RCP (J/Kg)	400	365	380	400	420

Table 4. Results of the structural characterization (phase observed, analyzed compositions, and lattice parameter of the $NaZn_{13}$, α-Fe, and LaFeSi phases) magnetic and magnetic entropy change for $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ (x = 0, 0.06, 0.12, 0.23, 0.34) [26].

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decrease from 197 K at x = 0 to 180 K at x = 0.06 and then increase to 185 K at x = 0.12 until 195 K at Cr concentration where x = 0.34. This variation of temperature occurs related to the more presence of α-Fe and LaFeSi phase (impurity) at lower Cr concentration and starts to decrease that amount by increasing Cr until x = 0.34, respectively. The variation of the T_C values with the Cr content in these compounds occurs according to two types of exchange interactions existing between Fe-Fe in the Fe-rich rare earth intermetallic compounds as discussed in detail somewhere else [26].

Magnetic hysteresis is one characteristic of the first-order magnetic transition as discuss in the previous section. It can be seen that the M-B curves exhibit almost no magnetic hysteresis for x = 0.34 which is found to be similar of the characteristic at x = 0 but did not change the first-order magnetic transition behaviour [26]. The phenomenon will provide the advantage of the sample with higher IEM transition and will contribute to enhance the value of magnetic entropy change [11, 23, 35].

4.3. Magnetocaloric effect

The values of $-\Delta S_M$ around T_C have been derived from the magnetic data and are indicated in **Table 4** for $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ compounds. $-\Delta S_M$ was found to decrease from 17 J kg^{-1} K^{-1} at x = 0 to 12 J kg^{-1} K^{-1} at x = 0.06 and then increase to 14.2 J kg^{-1} K^{-1} at x = 0.12 until it reaches 17.5 J kg^{-1} K^{-1} at x = 0.34 which is larger than Gd (10.2 J kg^{-1} K^{-1}). The relative cooling power (RCP) is defined by Eq. (3). It can clearly list at **Table 4** that the RCP values increase from 365 J kg^{-1} at x = 0.06 to 420 J kg^{-1} at x = 0.34 under 0–5 T field applied. The RCP value at x = 0.34 is slightly higher than the parent compound as indicated by the promising material of the $La_{0.7}Pr_{0.3}Fe_{11.06}Cr_{0.34}Si_{1.6}$ compound.

5. Conclusion

A systematic investigation of the structural and magnetic characterization of $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ for HTA and LTA samples has been carried out. The results show that the HTA offers more advantages in solving the problem of non-equilibrium solidification behaviour due to the incomplete peritectic reaction γ-Fe + L → La(Fe,Si)$_{13}$(τ_{1a}) that occurs in the LTA process. The HTA sample shows promising values of $-\Delta S_M$ with very small hysteresis loss. This indicates that the elevated temperature in HTA plays an important role to form the $NaZn_{13}$-type structure in the $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ compound.

Furthermore, the substitution of Cu for Fe in $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cu_xSi_{1.6}$ leads to a decrease the magnetic entropy change but eliminates hysteresis loss. Increasing the Cu concentration also changes the magnetic-phase transition type from first to second order which in effect reduces the characteristics of IEM transition. The Curie temperature, T_C, increases with increasing Cu concentration. This phenomenon is related with the increase in the lattice parameter and the modification of the composition. The compound with a small amount of Cu substitution shows a promising magnetic performance for magnetic refrigerator application, with no hysteresis loss and reasonable RCP.

In conclusion, substitution of Cr for Fe $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ compound leads to decreases in lattice parameter but variation behaviour on T_C. The variation of T_C with increasing Cr

concentration can be understood in terms of sensitive changes of Fe1-Fe2 and Fe2-Fe2 distances. Analysis of the magnetisation data demonstrates that the order of magnetic phase transition around T_C is consistent on the first-order type even when x = 0.34 for $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ compounds. Replacement of Fe by Cr leads to a reduction of the magnetic entropy change from x = 0 to x = 0.06; however, it starts to enhance again when one increases Cr concentration until x = 0.34.

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Author details

Muhamad Faiz Md Din[1,2]*, Jianli Wang[2] and Mohd Taufiq Ishak[1]

*Address all correspondence to: mfmd999@uowmail.edu.au

1 Department of Electrical and Electronic Engineering, Faculty of Engineering, National Defence University of Malaysia, Kuala Lumpur, Malaysia

2 Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW, Australia

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