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Effects of Cr substitution on structural and magnetic properties in La0.7Pr0.3Fe11.4Si1.6 compound

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Abstract

In an effort to explore the effect of substitution Fe by Cr in NaZn13-type La0.7Pr0.3Fe11.4–xCrxSi1.6 (x = 0, 0.06, 0.12, 0.26, and 0.34) compounds, the structure and magnetic properties have been investigated by high intensity of x-ray and neutron diffraction, scanning electron microscopy, specific heat, and magnetization measurement. It has been found that a substitution of Cr for Fe in this compounds leads to decrease in the lattice parameter a at room temperature but variation on Curie temperature (TC). While the first order nature of magnetic phase transition around TC does not change with increasing Cr content up to x = 0.34. High intensity x-ray and neutron diffraction study at variable temperatures for highest Cr concentration x = 0.34 confirmed the presence of strong magneto-volume effect around TC and indicated the direct evident of coexistence across magnetic transition as characteristic of first order nature. The values of $-\Delta S_M$ around TC decrease from 17 J kg−1 K−1 for x = 0 to 12 J kg−1 K−1 for x = 0.06 and then increases with further increasing Cr content up to 17.5 J kg−1 K−1 for x = 0.34 under a change of 0-5 T magnetic field. Similar behavior on relative cooling power which is decrease from 390 J kg−1 for x = 0 to 365 J kg−1 for x = 0.06 at the beginning and then increases up to 400 J kg−1 for x = 0.34. From the point of this view with the highest Cr concentration (x = 0.34) exhibits favourable material candidate for magnetic refrigerator application therefore should inspire further study concerning on higher Cr concentration in this compound.

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Effects of Cr substitution on structural and magnetic properties in $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ compound

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In an effort to explore the effect of substitution Fe by Cr in NaZn₁₃-type $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ (x = 0, 0.06, 0.12, 0.26, and 0.34) compounds, the structure and magnetic properties have been investigated by high intensity of x-ray and neutron diffraction, scanning electron microscopy, specific heat, and magnetization measurement. It has been found that a substitution of Cr for Fe in this compounds leads to decrease in the lattice parameter *a* at room temperature but variation on Curie temperature (T_C). While the first order nature of magnetic phase transition around T_C does not change with increasing Cr content up to x = 0.34. High intensity x-ray and neutron diffraction study at variable temperatures for highest Cr concentration x = 0.34 confirmed the presence of strong magneto-volume effect around T_C and indicated the direct evident of coexistence across magnetic transition as characteristic of first order nature. The values of $-\Delta S_M$ around T_C decrease from 17 J kg^{-1} K^{-1} for x = 0 to 12 J kg^{-1} K^{-1} for x = 0.06 and then increases with further increasing Cr content up to 17.5 J kg^{-1} K^{-1} for x = 0.34 under a change of 0–5 T magnetic field. Similar behavior on relative cooling power which is decrease from 390 J kg^{-1} for x = 0 to 365 J kg^{-1} for x = 0.06 at the beginning and then increases up to 400 J kg^{-1} for x = 0.34. From the point of this view with the highest Cr concentration (x = 0.34) exhibits favourable material candidate for magnetic refrigerator application therefore should inspire further study concerning on higher Cr concentration in this compound. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4868703]

The cubic NaZn₁₃-type $LaFe_{13-x}Si_x$ based compounds have been studied systematically since it provides many of advantage compare to other as magnetic materials for magnetic refrigerator application.[1,2] These based compounds exhibit large magnetocaloric effect (MCE) accompanied with first order magnetic transition (FOMT), soft ferromagnetism, and very low cost material.[3,4] The large value MCE can be ascribed from the effect of the itinerant-electron metamagnetic (IEM) transition around Curie temperature, T_C.[5] In order to increase MCE, change the suitable T_C and reduce the critical field of the 3*d*-metamagnetic transition in $LaFe_{13-x}Si_x$ compound as the rare-earth-Fe magnetic coupling display strong dependence on the type of rare-earth, doping other rare-earth element in La site has been studied.[6,7] However, these phenomena with first order magnetic transition usually were accompanied with thermal and magnetic hysteresis issues which contribute to bring hysteresis loss in detrimental the refrigerator capacity performance. Several studies have been done to solve this situation by the addition of substitution or interstitial atoms in $LaFe_{13-x}Si_x$ compounds.[8–12] From this point, we set the constant composition on rare-earth element and investigate the replacement Cr (atomic radius = 1.3 Å) for Fe (atomic radius = 1.26 Å) in $La_{0.7}Pr_{0.3}Fe_{13-x}Cr_xSi_x$ compounds on structure and magnetic properties in order to produce high potential magnetic material for magnetic refrigerator.

Polycrystalline ingots $La_{0.7}Pr_{0.3}Fe_{13-x}Cr_xSi_x$ were been prepare similar to previous study.[12] The crystal structures of the samples were checked by room temperature powder x-ray diffraction measurements with refined using the Fullprof software package, scanning electron microscopy (SEM), and energy dispersive spectrometer (EDS). The magnetic properties were investigated over the temperature range of 10–300 K using the vibrating sample magnetometer option of a Quantum Design 14 T physical properties measurement system (PPMS). The crystallographic and magnetic structural behaviors of $La_{0.7}Pr_{0.3}Fe_{11.06}Cr_{0.34}Si_{1.6}$ samples were investigated over the temperature range of 3–450 K by neutron powder diffraction experiments using the high intensity powder diffractometer Wombat (2.4205 Å) at OPAL, and high intensity x-ray diffraction (λ = 0.8265 Å) at Australian Synchrotron.

The room temperature x-ray diffraction (XRD) analysis in Table I shown that Cr concentration contributes to an increase the amount of α-Fe and LaFeSi phases from beginning x = 0.06 then decrease until x = 0.34 in $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ compounds. We suggest this behaviour may be related to bulk diffusion rate controlling factor of homogenization in cubic NaZn₁₃–type phase structure (space group *Fm3c*) by substitution Cr for Fe. From Table I, it can be seen that the

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TABLE I. Results of the structural characterization from room temperature XRD analysis and T_C for $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ compounds.

Nominal composition and T_C (K)	Phase	Wt. %	Lattice parameter, a (Å)	Atomic distance (Å) for	
				Fe1-Fe2	Fe2-Fe2
x = 0	NaZn$_{13}$	96.1	11.4585	2.4508	2.5522
(197 K)	α-Fe	3.5			
	LaFeSi	0.4			
x = 0.06	NaZn$_{13}$	85.9	11.4556	2.4506	2.5521
(180 K)	α-Fe	10.6			
	LaFeSi	3.5			
x = 0.12	NaZn$_{13}$	92.6	11.4540	2.4505	2.5517
(185 K)	α-Fe	6.0			
	LaFeSi	1.4			
x = 0.23	NaZn$_{13}$	94.0	11.4524	2.4501	2.5515
(190 K)	α-Fe	4.7			
	LaFeSi	1.3			
x = 0.34	NaZn$_{13}$	97.6	11.4518	2.4996	2.5511
(195 K)	α-Fe	2.3			
	LaFeSi	0.2			

weight fraction of the NaZn$_{13}$ structure decreases from 96% at x = 0 to 85% at x = 0.06 then increase to 97% with increasing Cr content till x = 0.34. The introduction of Cr into $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ 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 will be lowered agree well with Liu Xu *et al.*[13] That diffusion also sensitive to modification of both the electronic structure and lattice spacing[14] agrees with phenomena 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 different electronic environments (Fe $\sim 3d^6 4s^2$ and Cr $\sim 3d^5 4s^1$) in this study. This situation is proved by the high magnification SEM image in Figs. 1(a) and 1(b), which shows that the percentage of NaZn$_{13}$ phase for x = 0.34 is higher than x = 0.06 presence of the advantage in increasing Cr concentration. In order to justify the Cr element formed in NaZn$_{13}$ phase structure, EDS analysis has been performed and proved that Cr is formed as expected by using comparison for x = 0 and highest Cr concentration x = 0.34.

The temperature dependence of the magnetization of $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ compound is measured under
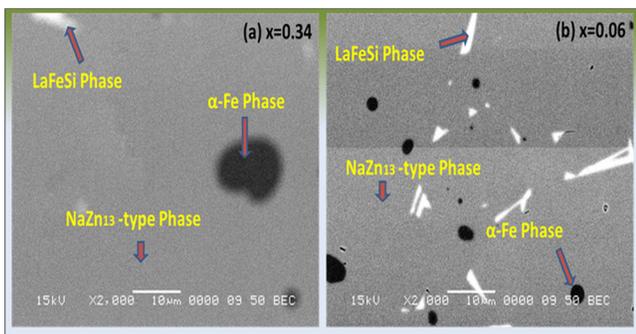

FIG. 1. High magnification backscattered SEM images of $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ samples: (a) x = 0.34 and (b) x = 0.06.

magnetic field of 0.01 T. The T_C shown in Table I was defined by the minimum of dM/dT.[15] T_C was found to decrease from 197 K at x = 0 to 180 K at x = 0.06 but start to increase to 185 K at x = 0.12 until 195 K at higher Cr concentration x = 0.34. We assume more presence of α-Fe and LaFeSi phase at lower Cr concentration contribute to variation in value of T_C as both of these phase are impurity. However, both of these phases are not critical as we found it did not change the first order phase transition behaviour compared to other study. The introduction of Cr into $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ 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 will be lowered agree well with Liu Xu *et al.*[13] The Fe1-Fe2 and Fe2-Fe2 distances have been obtained with the BLOKJE program[16] using the structural and positional parameters and listed in Table I. It can be seen clearly that the substitution of Cr for Fe leads to a decrease lattice parameter a, resulting in an decrement of Fe1-Fe2 and Fe2-Fe2 distance as confirmed the replacement Fe by Cr results in a dilution of magnetic atom (Fe) content.

Magnetization curves as a function of magnetic field up to 5 T for $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ (x = 0 and 0.34) have been measured under increasing and decreasing field at various temperatures and are shown in Figs. 2(a) and 2(b). It can be seen that the M-B curves exhibit almost no magnetic hysteresis for x = 0.34 which is found same of the characteristic at x = 0. Furthermore, it indicates that the field induced first order transition from paramagnetic to ferromagnetic was notably slightly increase by the introduction of Cr. The corresponding Arrott plots are drawn in Fig. 2(c) depicted the negative slopes in the isotherm Arrott plots indicate the first order nature of the phase transition around T_C according to I-S model for highest concentration x = 0.34.[4,17,18] It has been reconfirmed by others method (heat capacity measurement those that involve a latent heat) as shown in Fig. 2(d) and mixed peaks appear around Tc indicating the
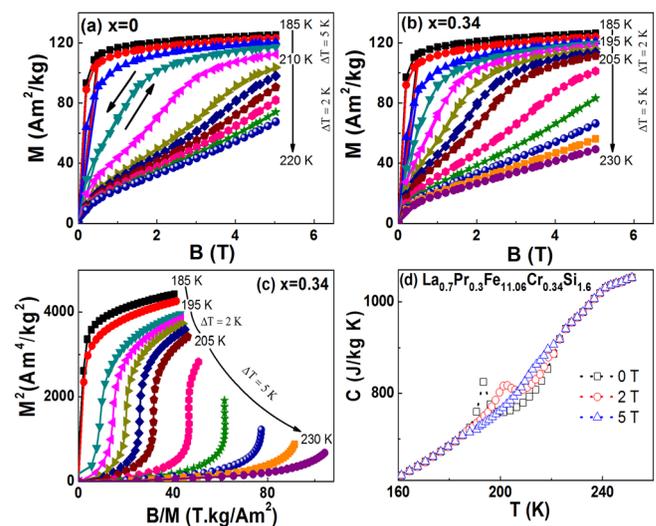

FIG. 2. Isothermal magnetization curves in the vicinity of the ferromagnetic ordering temperatures for: (a) $La_{0.7}Pr_{0.3}Fe_{11.4}Si_{1.6}$ and (b) $La_{0.7}Pr_{0.3}Fe_{11.06}Cr_{0.34}Si_{1.6}$; (c) Arrott plots of M^2 versus B/M and (d) heat capacity measurement for the set of $La_{0.7}Pr_{0.3}Fe_{11.06}Cr_{0.34}Si_{1.6}$.
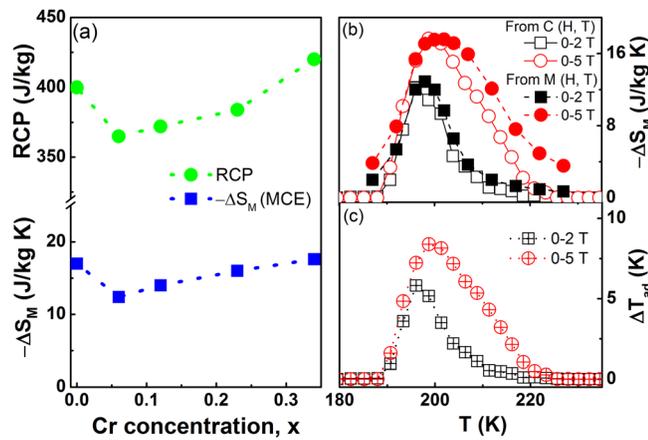
FIG. 3. (a) The RCP and $-\Delta S_M$ for $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ compounds. (b) The $-\Delta S_M$ determined from magnetization and heat capacity measurements and (c) The adiabatic temperature change for $La_{0.7}Pr_{0.3}Fe_{11.06}Cr_{0.34}Si_{1.6}$.
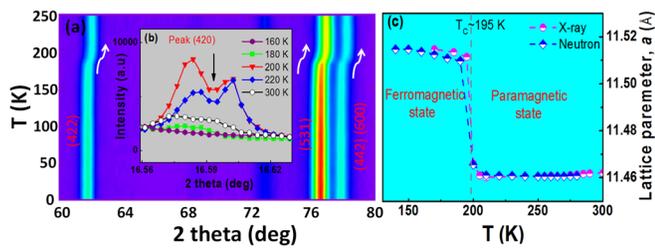

FIG. 4. (a) Neutron diffraction patterns for $La_{0.7}Pr_{0.3}Fe_{11.06}Cr_{0.34}Si_{1.6}$ over temperature range 10–250 K respectively and inside. (b) High intensity XRD pattern at selected temperature range 170–300 K. (c) The lattice parameters change around T_C of $La_{0.7}Pr_{0.3}Fe_{11.06}Cr_{0.34}Si_{1.6}$ compound.

coexistence of phases across magnetic transition defined by high intensity XRD as will discuss later.

The isothermal entropy change, $-\Delta S_M$, is defined from the magnetization curve by the Maxwell relation.[19] The values of $-\Delta S_M$ are shown in Fig. 3(a) as a function of temperature with a 0–5 T change in field for $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ compounds. $-\Delta S_M$ found to decrease from $17 \, J \, kg^{-1} \, K^{-1}$ at $x = 0$ to $12 \, J \, kg^{-1} \, K^{-1}$ at $x = 0.06$ increase to $14.2 \, J \, kg^{-1} \, K^{-1}$ at $x = 0.12$ until $17.5 \, J \, kg^{-1} \, K^{-1}$ at $x = 0.34$ which is larger than Gd ($10.2 \, J \, kg^{-1} \, K^{-1}$). It can be seen clearly that the $-\Delta S_M$ peak gradually becomes broader at higher temperature with increasing magnetic field from 2 to 5 T, which is a characteristic of the field induced IEM transition as shown for $x = 0.34$ in Fig. 3(b) and agree well with heat capacity measurement. The peak value of the adiabatic temperature change is derived to be $\Delta T_{ad}^{max} = 8.4$ K for $\Delta B = 0$–5 T and 5.5 K for $\Delta B = 0$–2 T as can be evaluated from $-\Delta S_M$ (T, B) and the heat capacity data as $\Delta T_{ad}(T,B) = \int_0^B \frac{T}{C_{B,P}} \left(\frac{\partial M}{\partial T} \right)_B dB$. The RCP as defined by the following formula:[9,20] $RCP = -\Delta S_M^{max} \delta T^{FWHM}$. It can be seen at Fig. 3(a) 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.

Neutron diffraction patterns indicated the shift of the peaks position to higher angle around T_C confirm the contraction of unit cell volume as shown in Fig. 4(a) and agree well with the XRD diffraction analysis in Fig. 4(b) together with coexistence of two phases (paramagnetic and ferromagnetic phases) across magnetic transition as indicator for first order magnetic behaviour. The variation in decrease of the lattice parameter, *a* was be found from 11.5148(3) Å at 170 K to 11.4608(2) Å at 200 K as depict in Fig. 4(c). The changes in lattice parameter at T_C according to magnetic state changes[21] indicate the presence of strong magneto-volume behaviour. It been found that around $-\Delta S_{structural} \sim 3.15 \, J \, kg^{-1} \, K^{-1}$ is estimated using the method from Gschneidner *et al.*[22] under $\Delta B = 0$–5 T.

In summary, substitution of Cr for Fe $La_{0.7}Pr_{0.3}Fe_{11.4-x}Cr_xSi_{1.6}$ compounds leads to decreases in lattice parameter but variation behaviour on T_C. Analysis of the magnetisation data demonstrates that the order of magnetic phase transition is consistent on first order type even $x = 0.34$. Replacement of Fe by Cr leads to a reduction of the magnetic entropy change from beginning at $x = 0$ to $x = 0.06$, however starts to enhance again when increasing Cr concentration until $x = 0.34$. High intensity neutron and x-ray diffraction studies demonstrate that $La_{0.7}Pr_{0.3}Fe_{11.06}Cr_{0.34}Si_{1.6}$ compound has contraction in unit cell from ferromagnetic to paramagnetic structure which contributes to produce high magnetic entropy change. However, this investigation is still incomplete as it will be the platform for us to further study, particularly further increase Cr concentration in this compound in order to confirm the ultimate of the beneficial in Cr substitution.

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