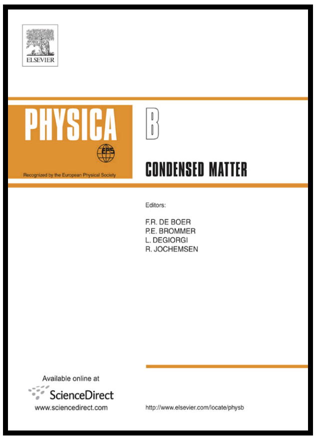

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Low Field Magnetocaloric Effect in Bulk and Ribbon Alloy La($Fe_{0.88}Si_{0.12}$)$_{13}$

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ABSTRACT

Low-field magnetocaloric effect occurred in itinerant metamagnetic materials is at core for magnetic cooling application. This works reports the magnetocaloric responses obtained at 1.35 T for the silicon-doped iron-based binary alloy La($Fe_{0.88}Si_{0.12}$)$_{13}$ in the bulk and ribbon form. Both samples possess a same symmetry but with different crystallite sizes and lattice parameters. The ribbon sample shows a larger maximum entropy change (nearly 8.5 times larger) and a higher Curie temperature (5 K higher) in comparison with that of the bulk sample. The obtained relative cooling power for the ribbon is also larger and very promising for application (RCP = 153 J/kg versus 25.2 J/kg for the bulk). The origin of the effect observed is assigned to the occurrence of negative magnetovolume effect in the ribbon structure with limit crystallization, caused by rapid cooling process at the preparation, which induced smaller crystallite size and large lattice constant at the overall local weaker crystal static field.

Keywords: Alloys, magnetocaloric effect, itinerant metamagnetism, La(Fe,Si)$_{13}$.

INTRODUCTION

The large magnetocaloric effect (MCE) appearing in the LaT_{13} alloys (T = Fe, Ni and Co), which exhibit the itinerant metamagnetic transition at near room temperature, has attracted considerable attention of researchers world-wide [1-4, 7], as the large values of MCE are essential for application of materials in novel gas-free magnetic cooling devices. In its nature, the MCE is a lowering of temperature of magnetic materials due to demagnetization, and when this happens at room temperature then it provides a feasible route to a new cooling technology, which does not involve the compressed gas and thus is absolutely environment friendly. In comparison with other materials having large MCE at near room temperature, such as the Ga-based alloys (e.g. $|-\Delta S_m|_{\max} \approx 8.5$ J/kgK in $Gd_5(Si_xGe_{1-x})_4$ in $T = 50 - 280$ K [2, 3, 5]), the LaT_{13} alloys are more preferred as they possess large contents of non-rare-earth metals which are more accessible than the expensive Ga. In the aspect of thermal stability, the LaT_{13} alloys are also very stable at high temperature so they can operate at higher temperature than that is allowed for the amorphous ribbons, the other good candidates for magnetic cooling, which is not stable in the high temperature range, however. Commonly, LaT_{13} alloys crystallize in a $NaZn_{13}$-type cubic structure with typical ferromagnetic arrangement [6-8]. Whereas this cubic arrangement is easily stabilized in $LaCo_{13}$ alloys due to high rigidity of Co bonding spheres, the same cubic structure can only be formed for $LaFe_{13}$ in the slightly doped pseudo-binary compounds of form $La(Fe_{1-x}M_x)_{13}$ with M = Al, Si [9, 10]. Because of presented high content of 3*d* metal (Fe) the doped compounds usually have high values of saturation magnetization and often express soft ferromagnetism. For the particular case of silicon-doped $La(Fe_{1-x}Si_x)_{13}$ alloys, as they exhibit a clear magnetovolume effect (MVE) near Curie temperature T_C (which is believed to be associated with the itinerant metamagnetic transition at the same temperature), the role of the pressure-induced change of T_C, either by doping of H and C (causing a cell expansion, which is equivalent to a negative pressure effect) or by applying of hydrostatic pressure (causing a cell compression, or alias positive pressure effect), was investigated and reported in several studies previously [11-13, 18]. There appeared that the Curie temperature T_C, and simultaneously with it, the reduction of the critical field of itinerant metamagnetic transition, could be achieved by doping of La by other magnetic rare-earths, such as Ce, Gd, Nd and Pr [14-17], or even by excessive adding of La itself [18].

The $La(Fe_{0.88}Si_{0.12})_{13}$ compounds were reported in Refs. [14, 16, 25-27] where the readers can find the T_C = 195 K [26], 197 K [16], 202 K [27], and 210 K [14]; the magnetic entropy change (at the high field of 5 T) $|-\Delta S_m|_{max}$ = 4.80 J/kg·K [14], 20.0 J/kg·K [26] and 12.5 J/kg·K [16]. There was reported a mere variation of lattice constant for the above cases from 11.458 [14] to 11.477 Å [16]. As presented, although the achieved $|-\Delta S_m|_{max}$ values are quite high and feasible for direct application usage, the involvement of a very high field practically limit the range of real application.

Thus, for the purpose of achieving high values of magnetic entropy change while preserving the low field variation ($\Delta H \leq 1.5$ T) we studied the alloy of modified content $La(Fe_{0.88}Si_{0.12})_{13}$ in both bulk and ribbon forms, and present here the obtained MCE at low applied field ΔH = 1.35 T in order to compare their magnetocaloric properties at varying structural conditions, which in turn may shed light onto the origin of MCE in these compounds.

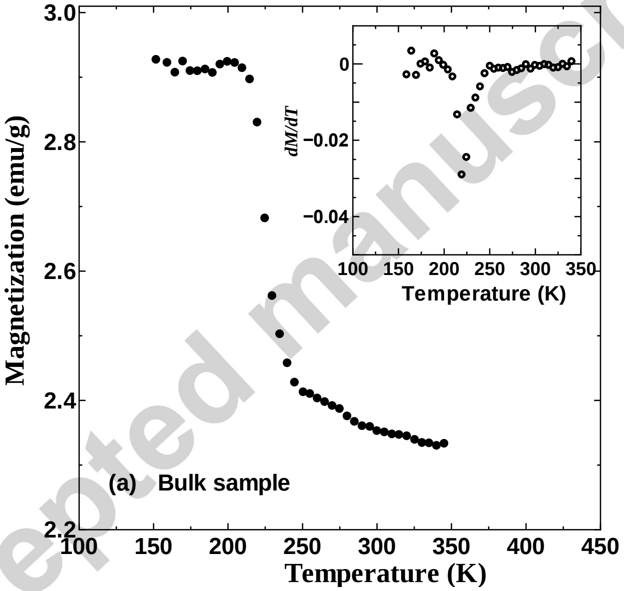
EXPERIMENTAL

The bulk samples $La(Fe_{0.88}Si_{0.12})_{13}$ (alias $LaFe_{11.44}Si_{1.56}$) were prepared from the stoichiometric mixture of the precursor metals La, Fe (3N) and Si (5N) by mean of arc-melting technique in Argon gas atmosphere. The ribbon samples with thickness from 12 to 15 µm were prepared by using a rapid cooling technique on a single copper wheel of diameter d = 200 mm (Melt Spinner SC system), which rotated with a surface speed of 35 m/s in vacuum (10^{-5} Torr). The samples were then sintered in vacuum (10^{-5} Torr) at 1100°C for 7 days. The structures of samples were analyzed by X-ray diffraction technique using a Bruker D5000 diffractometer and the magnetic properties, including

MCE, were investigated using a Vibrating Sample Magnetometer with a maximum applied field of 13.5 kOe (VSM on DMS 880 Instrument).

RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependences of magnetization of La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ for the bulk (a) and ribbon (b) samples, as measured at applied field H = 100 Oe. As observed, the maximum magnetizations for the bulk and ribbon are ~ 2.9 and 47 emu/g respectively.



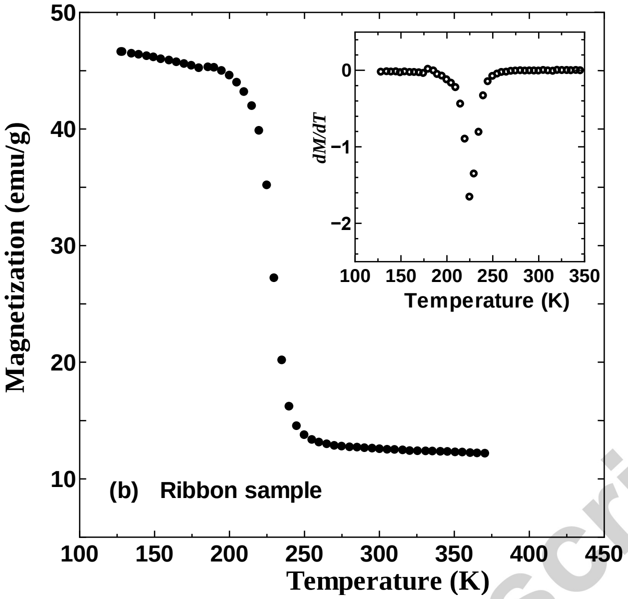


Fig. 1. The dependence of magnetization on temperature for La$(Fe_{0.88}Si_{0.12})_{13}$ samples (a) the bulk and (b) the ribbon. The data were recorded at a constant applied field H = 100 Oe. The insert in each graph shows a plot of derivation curve $\partial M/\partial T(T)$.

The transition temperatures from the ferromagnetic ordering state to paramagnetic state (Curie temperature T_C) can be determined from the maxima of the derivation curves $\partial M/\partial T(T)$ (plots showed in the insets of Fig. 1). The corresponding values are T_C = 220 K for the bulk and 225 K for the ribbons. Fig. 1 also shows that, for the temperature above T_C, the remaining magnetization prevails at 2.3 for the bulk and 12 emu/g for the ribbon.

The structure characterization of samples has been taken in term of Rietveld analysis [19] of phase for $NaZn_{13}$-type structure (the details of a similar analysis is available in Ref. [18]). The obtained results showed that both bulk and ribbons possess a well-defined single phase $Fm\overline{3}m$ cubic structure, with traces of α-Fe phase being seen in both cases. The lattice parameter for the ribbon is a little bit higher (11.474 Å) in comparison with the one of the bulk sample (11.466 Å) and both values fall within the observed range of lattice parameters for La$(Fe_{0.88}Si_{0.12})_{13}$.

The amount of α-Fe phase was significantly larger in the bulk sample in comparison with that of the ribbon. This probably originates in a limit diffusion time and also a limit thermal supply in a rapid cooling process which prohibits a larger growth of α-Fe phase. The subsequent sintering process did not effect the further growth of this phase in the ribbon samples. This observation also agrees with larger crystallite size observed for the bulk (37 nm) in comparison with that for the ribbon (18 nm). It is worth to note about the 5K rise of T_C for the ribbon (220 versus 225 K) in the correspondence with the smaller crystallite size and larger lattice parameter of the ribbon sample: a smaller crystallite size is equivalent to a smaller crystal field, which means practically an expansion of the lattice due to a lack of Coulomb attraction in the small lattice. This in turn induces a larger negative magnetovolume effect in the ribbon in comparison with that effect in the bulk, and as discussed in Ref. [18], a negative magnetovolume effect induces a higher T_C. An inversed process of reducing T_C was frequently observed when a lattice was compressed due to applied hydrostatic pressure (positive MVE).

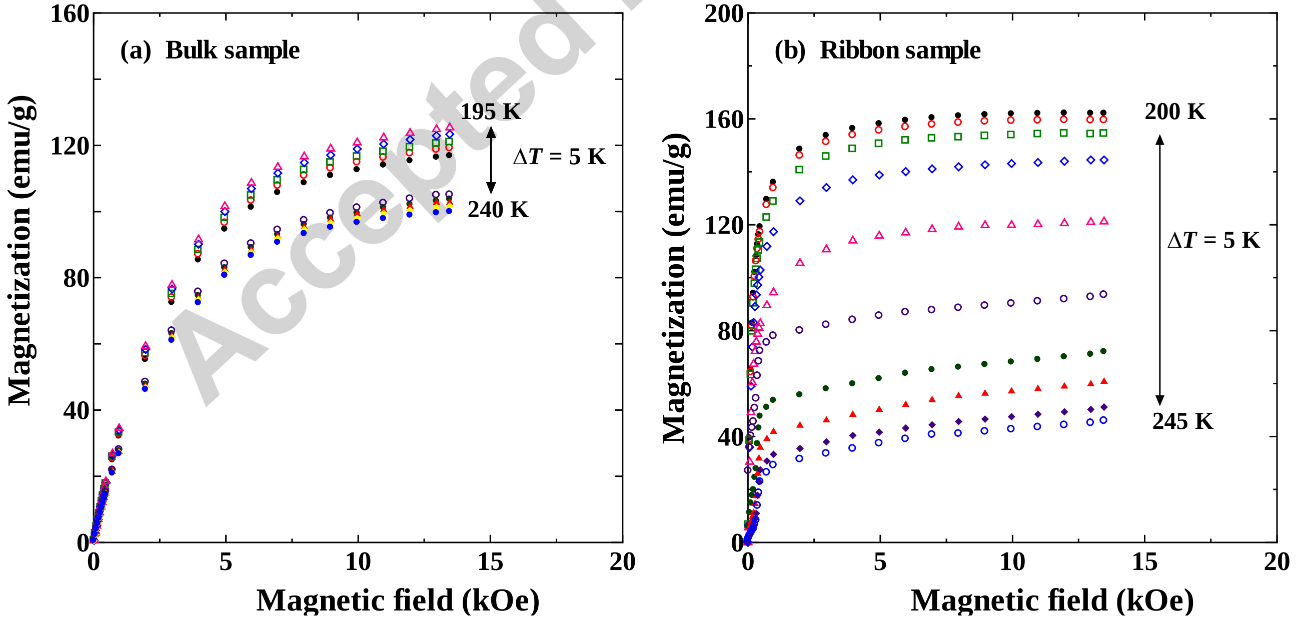


Fig. 2. Magnetization isotherms recorded at ΔH = 1.35 T for $La(Fe_{0.88}Si_{0.12})_{13}$ samples: the bulk (a) and the ribbon (b).

Fig. 2 shows the corresponding isothermal magnetization curves recorded in the variation of applied magnetic field ΔH from 0 to 1.35 T, as obtained for the bulk and the ribbon samples in the temperature range across the T_C, that is from 190 to 245 K. Visibly, the ribbon sample shows a more rapid change of magnetization according to applied field. The change of magnetic entropy can be evaluated by using the following Maxwell equation [22]:

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \tag{1}$$

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

$$\Delta S_m \approx \frac{1}{\Delta T}\left[\int_0^H [M((T+\Delta T),H) - M(T,H)]dH\right] \tag{3}$$

The results of ΔS are showed in Fig. 3, where the peaks of maximal entropy changes ($-\Delta S_m$) are found around the T_C: $|-\Delta S_m|_{max}$ = 1.2 for the bulk (T_C = 220 K) and 10.2 J/kgK for the ribbons (T_C = 225 K). For comparison, the $|-\Delta S_m|_{max}$ obtained for 20% Ce-doped $LaFe_{11.44}Si_{1.56}$ [16] was 18.67 J/kgK at ΔH = 4T, therefore the value $|-\Delta S_m|_{max}$ = 10.2 J/kgK (at 1.35 T) for the ribbon is quite considerable.

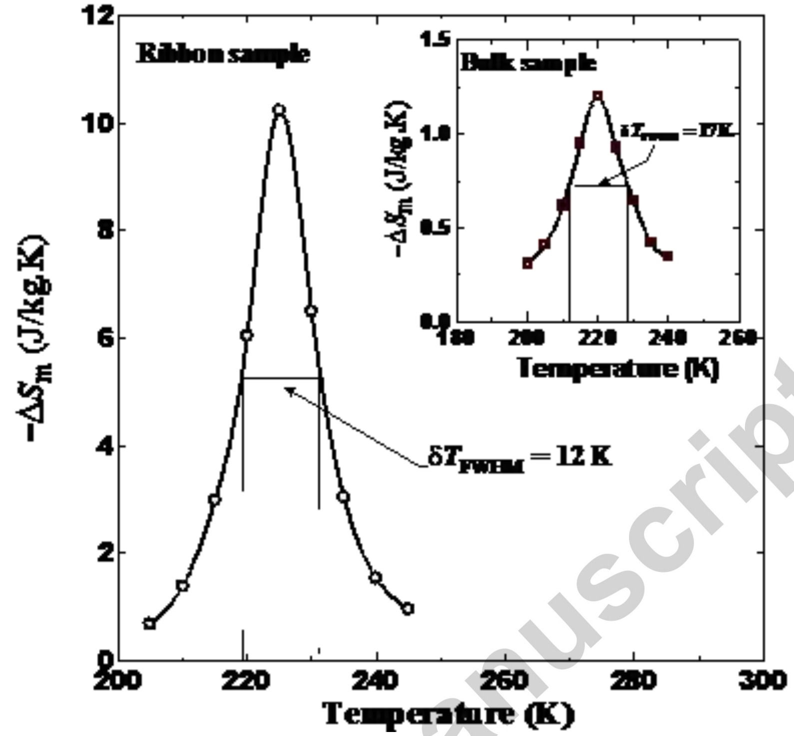


Fig. 3. Dependence of isothermal magnetic entropy change $-\Delta S_m$ on temperature for the La$(Fe_{0.88}Si_{0.12})_{13}$ ribbon sample (result for the bulk sample is showed in the inset).

However, the value of full-width-at-half-maximum (δT_{FWHM}), which is significant for the cooling power of particular materials, is a little better for the bulk (17 K) in comparison with that of the ribbon (12 K).

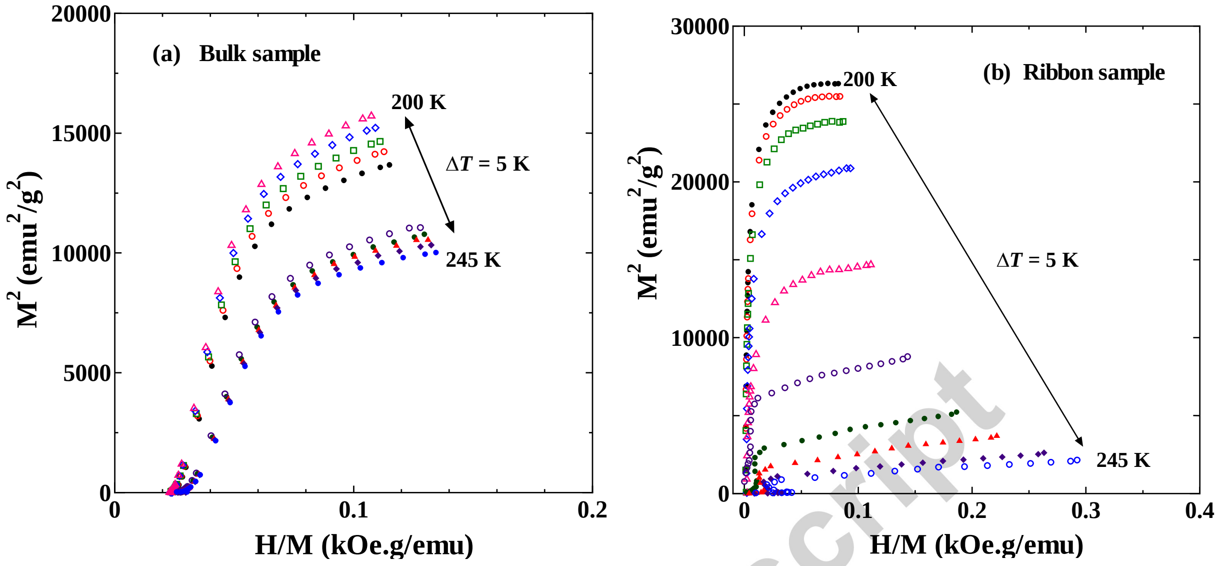


Fig. 4. The Arrot plots for La$(Fe_{0.88}Si_{0.12})_{13}$ samples: (a) the bulk and (b) the ribbon

The relative cooling powers (RCP), defined as RCP = $|-\Delta S_m|_{max} \times \delta T_{FWHM}$ [18, 23, 24], and calculated accordingly using the above values of δT_{FWHM} are 25.2 J/kg for the bulk and 153 J/kg for the ribbon. The RCP of the ribbon, which is large enough among the known Si-doped $LaFe_{13}$ compounds, is very promising for direct application usage. For examples, the RCP of a La-excess self-doped compound $La_{1.06}(Fe_{0.85}Si_{0.15})_{13}$ at ΔH = 2 T was around 108 J/kg, as deduced from the data given in Ref.[18] (although this compound gave RCP = 418 J/kg at ΔH = 7 T).

To investigate the nature of structural transition, corresponding to a change in magnetic ordering near Curie temperature, we studied the Arrot plots of the bulk and the ribbon. For this purpose, the measured $M(H)$ isotherms were transformed into the H/M versus M^2 plots, where a negative slope is commonly recognized as significant for the first-order magnetic transition (also referred to as the Banerjee criterion) [21]. The results for bulk and ribbon samples are featured in Fig. 4, from which we may easily recognize the negative values for the slopes for both bulk and ribbon samples. As the values of slopes are larger for the ribbon, a larger structural transition occurred for this sample, and this observation agrees well with a larger MCE value that has been observed (*i.e.* $|-\Delta S_m|_{max}$ = 10.2 J/kgK in comparison with 1.2 J/kgK for the bulk).

It is known that in the Si-doped $LaFe_{13}$ family the characteristics of the first-order itinerant metamagnetic transition including T_C and $-\Delta S_m$ involve with both applied magnetic field and applied hydrostatic pressure. For the systems exhibiting magnetovolume effect the pressure has substantial effect on increasing $-\Delta S_m$, but it does so for the cost of reducing T_C. When the lattice compresses the T_C always decreases. Thus, the intuitive route to higher T_C while still preserving large $-\Delta S_m$ is to manipulate a so-called negative magnetovolume effect (negative pressure) by doping of the third elements (*e.g.* H, C, Ce, La...) so that the lattice will expand. In the agreement with this consideration, the obtained better T_C, $-\Delta S_m$ and RCP for the ribbon sample may be understood: the origin is just a better magnetovolume effect in the ribbon due to smaller crystallite size, and a corresponding lower local crystal field, which in turn expands the lattice and induces a negative magnetovolume effect. However, it is difficult on the pure phenomenological basis to fully explain the suggested MVE in our ribbon sample. To do so one will need the detailed modeling and simulation on quantum theory level, and we leave this for future consideration.

CONCLUSION

We show that the same compound $La(Fe_{0.88}Si_{0.12})_{13}$ prepared under different routes exhibits different structural characteristics and different magnetocaloric responses. It is desirable that the ribbon sample shows both higher Curie temperature T_C (225 K) and larger maximum magnetic entropy change $|-\Delta S_m|_{max}$ (10.2 J/kgK, nearly 8.5 times larger in contrast to that of the bulk), together with a promising value of RCP (153 J/kg), obtained at low field variation (ΔH = 1.35 T). It was found that both bulk and ribbon attributed to the occurrence of a first-order itinerant metamagnetic transition, and it was clear that the measure of the magnetocaloric responses upon this transition was better for the ribbon in comparison with the bulk. The reason for this behavior may be found in the negative magnetovolume effect that occurs in the ribbon due to limit crystallization caused by rapid cooling process.

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