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*Published in:*
3rd International Conference on Magnetic Refrigeration at Room Temperature

*Publication date:*
2009

# CHARACTERIZATION STUDY OF A PLATE OF THE MAGNETO-CALORIC MATERIAL $La(Fe,Co,Si)_{13}$

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## ABSTRACT

A sample of magnetocaloric material with nominal composition $La(Fe_{0.851}Co_{0.066}Si_{0.083})_{13}$ is shown to present a ferromagnetic-to-paramagnetic transition with a Curie temperature of $T_C$ = 278.7 K. Isothermal magnetization curves were used to determine the volumetric magnetic entropy change, $\Delta S_M$(mJ/cm$^3$K). The values thus found are compared to those of Gd and found to be almost twice as large for a given field. Hysteresis curves and thermomagnetic data show that a slight thermal hysteresis of 2 K is present, while no magnetic hysteresis exists in this material. Therefore, we show that several of the disadvantages previously associated with $NaZn_{13}$-structured materials are not present in $La(Fe,Co,Si)_{13}$ materials produced by powder metallurgy.

## 1. INTRODUCTION

A number of magnetocaloric materials series are currently being studied for the purpose of magnetic refrigeration near room temperature, where the material will play the role of refrigerant. One such series is $La(Fe,Co,Si)_{13}$ (see e.g. Liu and Altounian 2003, Ilyn et al. 2005), which has the $NaZn_{13}$ structure. Other material series with the same structure are e.g. $La(Fe,Si)_{13}$ and $La(Fe,Al)_{13}$. These materials display a variety of magnetic states and transitions. $La(Fe,Si)_{13}$ shows a first-order ferromagnetic transition and a field-induced itinerant-electron magnetic transition (Fujieda et al. 2002, Fujita et al. 2001, Palstra et al. 1983), whereas $La(Fe_xAl_{1-x})_{13}$ for $x > 0.86$ is an antiferromagnet (Palstra et al. 1985). This variety has made the $NaZn_{13}$-structured materials interesting, some of them for magnetic refrigeration. The disadvantages of the magnetocaloric $NaZn_{13}$-structured materials, when compared to the benchmark material Gd, have been fabrication, shape processing, size of the adiabatic temperature change ($\Delta T_{ad}$), hysteresis, corrosion and brittleness (Gschneidner et al. 2008). In this paper, we present the results of a characterization study on a sheet of $La(Fe,Co,Si)_{13}$, which was fabricated using a powder metallurgical production route that can be utilized for large scale production (Katter et al. 2008).

## 2. SAMPLE PREPARATION

The sample was prepared by Vacuumschmelze GmbH using a novel production method significantly reducing the preparation time compared to arc-melting and subsequent heat treatment, the standard method for obtaining bulk samples of $La(Fe,Co,Si)_{13}$. Initially, commercial powders of elemental Fe and Si were mixed with coarse powders of $LaH_x$ as well as various La-Fe-Co-Si master alloys. The mixture was milled in kg quantities in a jet mill under inert gas to a particle size of <5 μm as measured by a Fisher Sub-Sieve Sizer (FSSS). The powders, which were shown by the sieve analysis to contain particles < 32 μm, were then compacted in a die with an applied pressure of about 400 MPa (4 t/cm$^2$). Following this, the green parts were sintered at temperatures between 1333 K and 1433 K for 4 to 8 hours under inert conditions. The sample composition was determined by the manufacturer using X-ray Fluorescence Analysis (XFA) and the density was measured using the Archimedes principle to find a value of 6.98 g/cm$^3$. According to the TDR (Thermally induced Decomposition and Recombination) process (Katter et al. 2009) the sintered die-pressed blocks were heat treated at about 1073 K to decompose the $La(Fe,Co,Si)_{13}$ phase and improve their

machinability. This allowed the sample to be cut to the required shape (a plate) by conventional wire Electrical Discharge Machining (EDM). The sample was then rehomogenized at about 1323 K to recombine the $La(Fe,Co,Si)_{13}$ phase. The prepared sample was a plate measuring 20 × 25 × 0.9 mm, which was subsequently cut using a table top cut-off machine into smaller samples suitable for experiments.

## 3. EXPERIMENTAL

X-ray diffractograms were obtained on a Bruker D8 Advance Diffractometer using Cu $K_\alpha$ radiation. Rietveld refinement of the experimental data allowed for the determination of phases and lattice constants using the program FullProf (Rodriguez-Carvajal 1993). Magnetization measurements were carried out using a LakeShore 7407 Vibrating Sample Magnetometer (VSM). Isothermal magnetization measurements as a function of field were made at a ramp rate of 30 Oe/s, a rate low enough to cause only minor heating (~ 0.2 K) in the sample during application of the field, in applied fields up to $\mu_0 H$ = 1.6 T. Magnetization measurements as a function of temperature at low applied fields of 85 Oe were made as point-by-point measurements in steps of 1 K and with a measurement time of 4 s/point. Calorimetric data in applied fields up to 1 T were obtained using a novel Differential Scanning Calorimeter (DSC) (Jeppesen et al. 2008).

## 4. RESULTS

The X-ray diffraction pattern confirms that the main phase in the prepared sample has crystallized in a cubic $NaZn_{13}$ structure. A nominal composition of the sample, $La(Fe_{0.851}Co_{0.066}Si_{0.083})_{13}$, was determined beforehand by the manufacturer of the sample using XFA. However, two cubic phases were identified in the sample: $La(Fe,Co,Si)_{13}$ (space group: *Fm3c*) and α-Fe(Co,Si) (*Im3m*). Surprisingly, no peaks corresponding to LaFeSi (*P4/nmm*) are present. The information extracted from the X-ray diffraction analysis is given in Table 1. In addition to the two identified phases, peaks are seen at low scattering angles, which could not be identified, see Fig. 1. The unidentified phase(s) is/are considered to be present in small quantities. As no knowledge of the crystallite sizes was at hand, the microstructural analysis leading to the stated weight percentages did not take into account the possibility of differing absorption contrast factors (Brindley coefficients).

Table 1. Data for phases identified in sample from X-ray diffraction and subsequent Rietveld refinement.

| | This paper | Comparison value | Reference |
|---|---|---|---|
| $La(Fe,Co,Si)_{13}$ | | | |
| Lattice parameter | 11.506 Å | ~11.50 Å | (Hu et al. 2005) |
| Weight percentage | 95 (2) | | |
| α-Fe(Co,Si) | | | |
| Lattice parameter | 2.869 Å | 2.8604(5) Å | (Basinski et al. 1955) |
| Weight percentage | 5.1 (3) | | |

Because impurities are present in the sample and the composition was determined using XFA, the actual composition of the $La(Fe,Co,Si)_{13}$ phase is known to differ slightly from the nominal one. The lattice parameters determined for the two cubic phases at room temperature are in good agreement with previously published values (Hu et al. 2005, Basinski et al. 1955). α-Fe is ferromagnetic with a transition temperature of 1043 K (Tauer and Weiss 1955) and could therefore interact magnetically with the other phases via exchange or dipole interaction. However, we consider this effect of the α-Fe phase negligible.

Thermomagnetic data recorded in an applied field of 85 Oe are presented in Fig. 2. The data was recorded for both increasing and decreasing temperature, and for increasing temperature both field-cooled (FC) and zero-field-cooled (ZFC) data is shown. The magnetization in the ferromagnetic state is slightly higher after field-cooling, but the paramagnetic-to-ferromagnetic transition follows closely that of the zero-field-cooled one. The experimental data shows that a small thermal hysteresis of 2 K is present and that the sample orders at a higher temperature upon cooling.

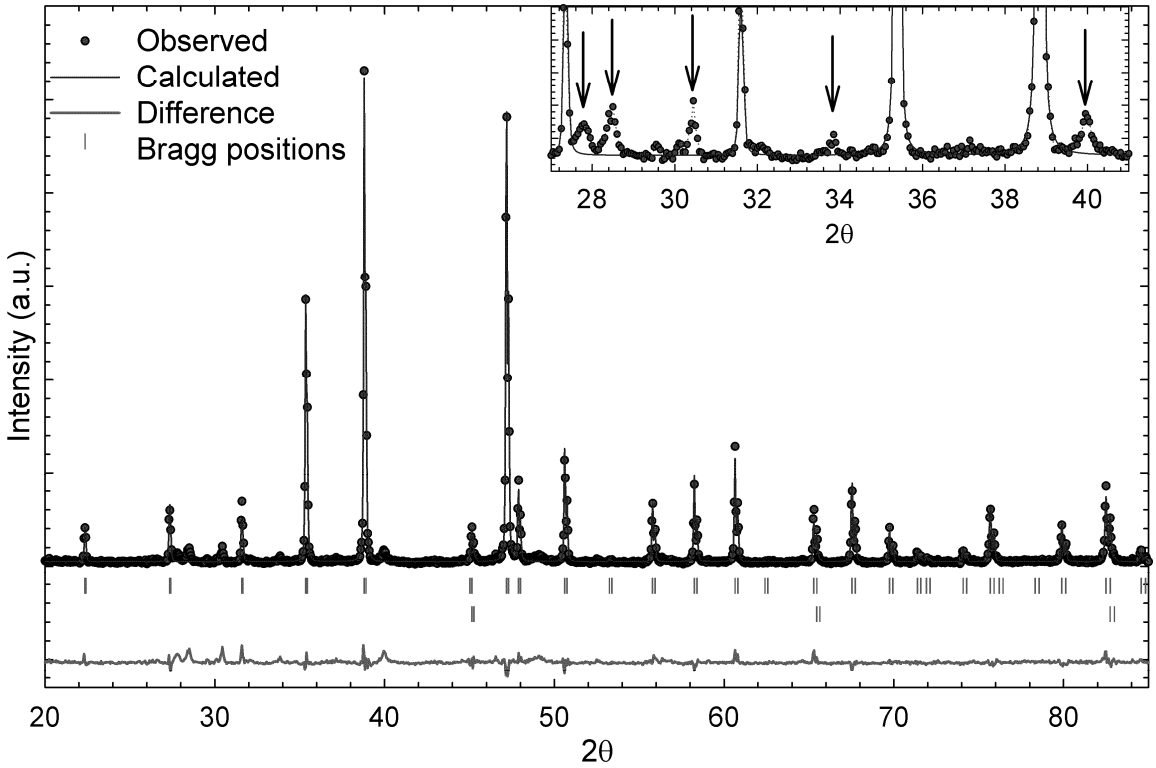


Figure 1. X-ray diffractogram of the $La(Fe,Co,Si)_{13}$ sample at room temperature. The inset shows unidentified peaks at low scattering angles.

Using the formula for the demagnetization in a rectangular prism (Aharoni 1998), the average internal fields were calculated. The low-field susceptibility, $\chi$, at an internal field of 150 Oe was extracted from the isothermal initial curves recorded with increasing temperature and is shown in Fig. 2 for temperatures above that of the magnetic transition. In the paramagnetic phase, the susceptibility was fitted to the Curie-Weiss formula,

$$\chi \propto \frac{C}{T - T_c}. \qquad (1)$$

By fitting the susceptibility for $T \geq 280$ K to Eq. (1) we find $T_C = 278.7$ K.

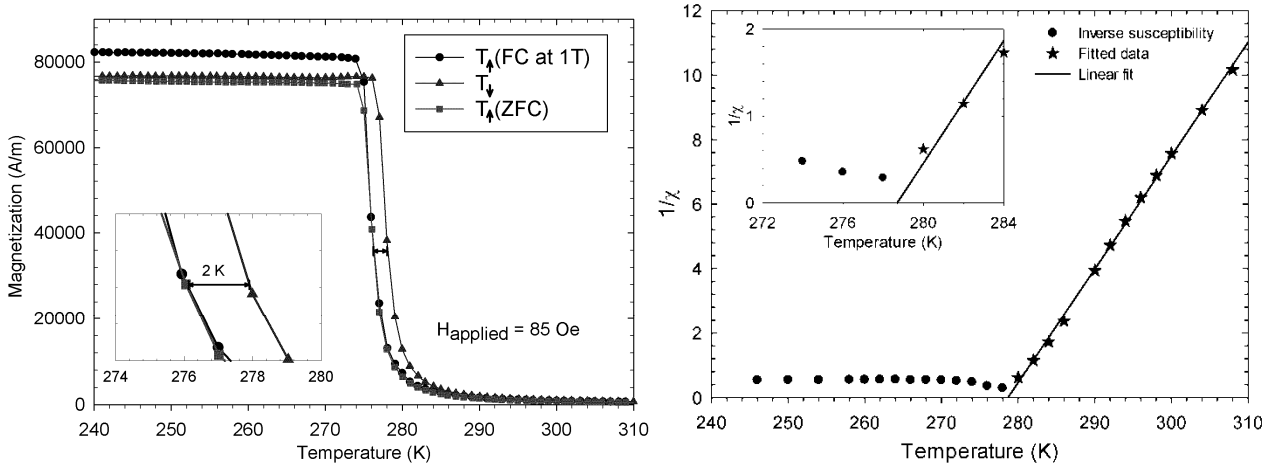


Figure 2. (left) Magnetization as a function of temperature recorded with an applied field of 85 Oe. A thermal hysteresis of 2 K is apparent and shown in more detail in the inset. (right) Magnetic susceptibility as a function of temperature. From the fit a Curie temperature of 278.7 K is found.

The magnetic entropy change, $\Delta S_M(T,\Delta H)$, was calculated using the equation,

$$\Delta S_M(T,\Delta H) = \mu_0 \int_0^H \left( \frac{\partial M}{\partial T} \right)_{H,p} dH, \qquad (2)$$

where $T$ and $H$ are the temperature and the magnetic field, respectively. Fig. 3 shows the calculated $\Delta S_M$ as a function of temperature for a selection of internal fields as well as a mesh plot of the magnetic entropy change for all recorded temperatures and internal fields. In Table 2 selected values of $\Delta S_M$ are given in different units, compared to the results from two different Gd samples. One Gd sample is a commercial grade Gd, while the purity of the other is unknown. As values of magnetic entropy change given in papers are usually for applied fields and not internal fields, both are given to aid in comparing the values.

Table 2. Selection of maximum values of magnetic entropy changes, $\Delta S_M$, determined from isothermal magnetization measurements for a selection of applied and internal magnetic fields.

| Applied field, $\mu_0 H$ (T) | 0.75 | 1.00 | 1.25 | 1.50 |
|---|---|---|---|---|
| $La(Fe,Co,Si)_{13}$ sample under study | | | | |
| $\Delta S_{M,max}$(mJ/cm$^3$·K) | 34.3 | 43.5 | 52.3 | 60.3 |
| $\Delta S_{M,max}$(J/mol·K) | 4.0 | 5.2 | 6.3 | 7.2 |
| $\Delta S_{M,max}$(J/kg·K) | 4.9 | 6.2 | 7.2 | 8.2 |
| Gd (own reference sample, commercial grade) | | | | |
| $\Delta S_{M,max}$(mJ/cm$^3$·K) | 17.3 | 22.4 | 26.9 | 31.2 |
| $\Delta S_{M,max}$(J/mol·K) | 0.3 | 0.4 | 0.5 | 0.6 |
| $\Delta S_{M,max}$(J/kg·K) | 2.2 | 2.8 | 3.4 | 3.9 |
| Gd (Gschneidner et al 2000) | | | | |
| $\Delta S_{M,max}$(mJ/cm$^3$·K) | - | 23.7 | - | 33.1 |
| Internal field, $\mu_0 H_i$ (T) | 0.75 | 1.00 | 1.25/1.20 | 1.46 |
| $La(Fe,Co,Si)_{13}$ sample under study | | | | |
| $\Delta S_{M,max}$(mJ/cm$^3$·K) | 36.4 | 45.8 | 54.6 | 61.2 |
| $\Delta S_{M,max}$(J/mol·K) | 4.4 | 5.5 | 6.5 | 7.3 |
| $\Delta S_{M,max}$(J/kg·K) | 5.2 | 6.6 | 7.8 | 8.7 |
| Gd (own reference sample, commercial grade) | | | | |
| $\Delta S_{M,max}$(mJ/cm$^3$·K) | 21.2 | 25.3 | 29.4 | - |
| $\Delta S_{M,max}$(J/mol·K) | 0.4 | 0.5 | 0.6 | - |
| $\Delta S_{M,max}$(J/kg·K) | 2.7 | 3.3 | 3.7 | - |

In the figures, we present $\Delta S_M$ in volumetric units as it is desirable for the purpose of magnetic refrigeration to have the largest entropy change in the smallest volume. From the data presented we see that the sample of $La(Fe,Co,Si)_{13}$ has a higher maximum value of volumetric entropy change than that of the benchmark material Gd. It is well known that when the material series of $La(Fe,Co,Si)_{13}$ is doped to increase the transition temperature, the magnetic entropy change decreases (Hu et al. 2005). However, $\Delta S_M$ would not be expected to be halved for a shift in temperature of 20 K. The values of the gravimetric magnetic entropy change, $\Delta S_M$ (J/kgK), for our sample with nominal composition $La(Fe_{0.851}Co_{0.066}Si_{0.083})_{13}$ compares well with previously published values (Hu et al 2005) for $La(Fe_{0.860}Co_{0.055}Si_{0.085})_{13}$.

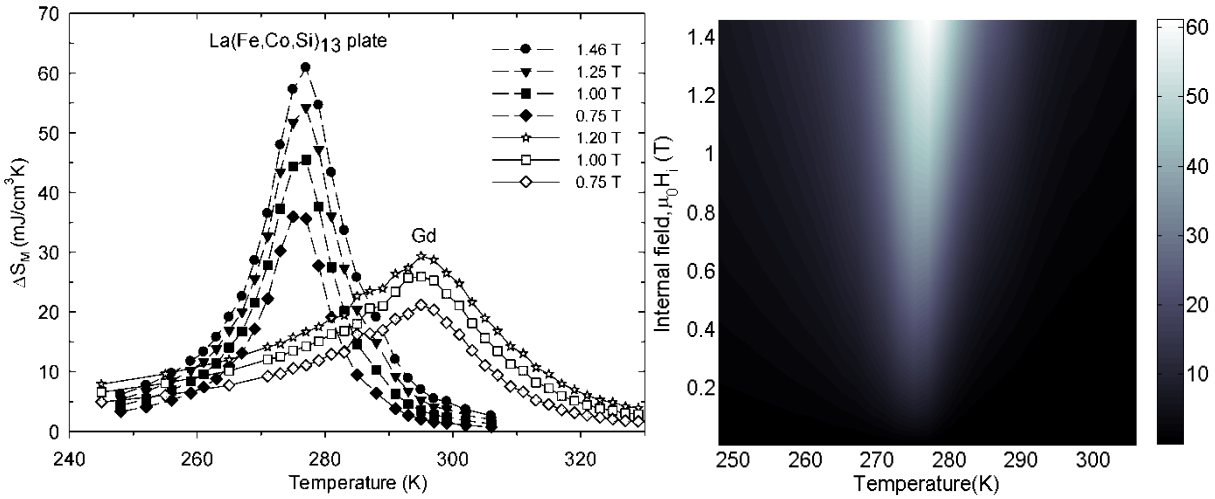


Figure 3. (left) The volumetric magnetic entropy change, $\Delta S_M$, as a function of temperature for a selection of internal fields, $\mu_0 H_i$. Values for a sample of the benchmark material Gd is shown for comparison with that of the $La(Fe,Co,Si)_{13}$ sample. (right) The volumetric magnetic entropy change, $\Delta S_M$ (mJ/cm$^3$K) for all internal fields and temperatures. The data was plotted using an interpolating function.

Hysteresis curves near the transition temperature show no magnetic hysteresis, see inset of Fig. 4. A slight opening of the curve is seen in the data recorded near the transition temperature due to heating of the sample (~0.1 K) when the magnetic field is ramped for the measurements, i.e. due to the magnetocaloric effect itself.

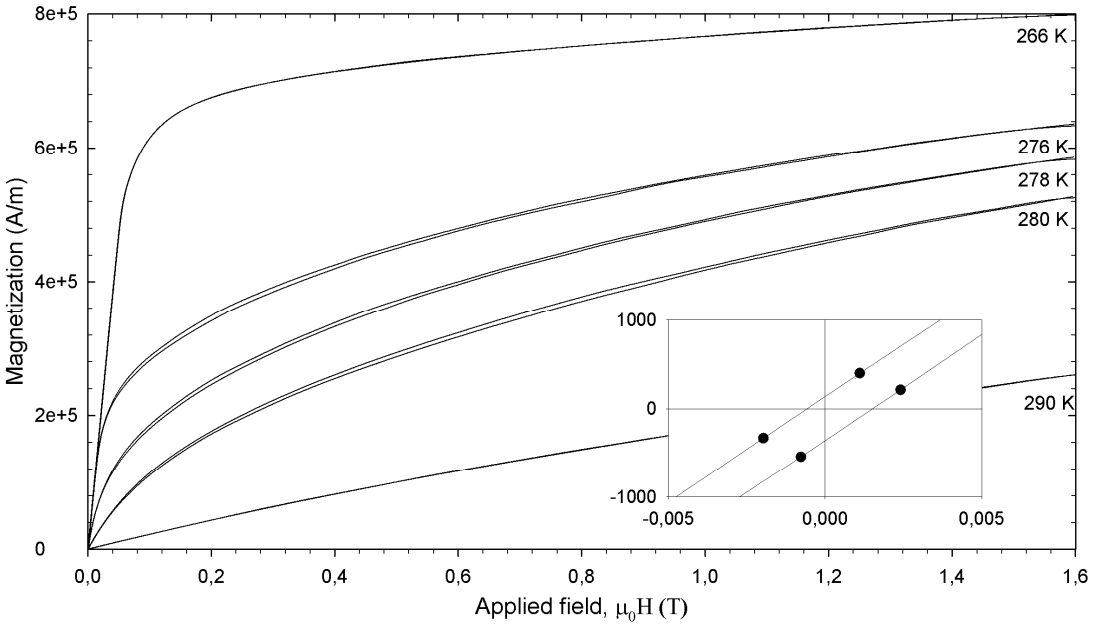


Figure 4. Hysteresis curves recorded at temperatures around that of the magnetic transition. Curves recorded near the transition temperature show a slight opening due to the magnetocaloric effect. Data near the origin is shown in the inset and from this it is clear that no magnetic hysteresis is present in the sample.

The heat capacity, $c_p$, of the sample was calculated from DSC measurements in a series of applied magnetic fields, see Fig. 5. With increasing applied field the peak in $c_p$ shifts to higher temperatures and broadens. In future work this data will be used to calculate the adiabatic temperature change, $\Delta T_{ad}$.

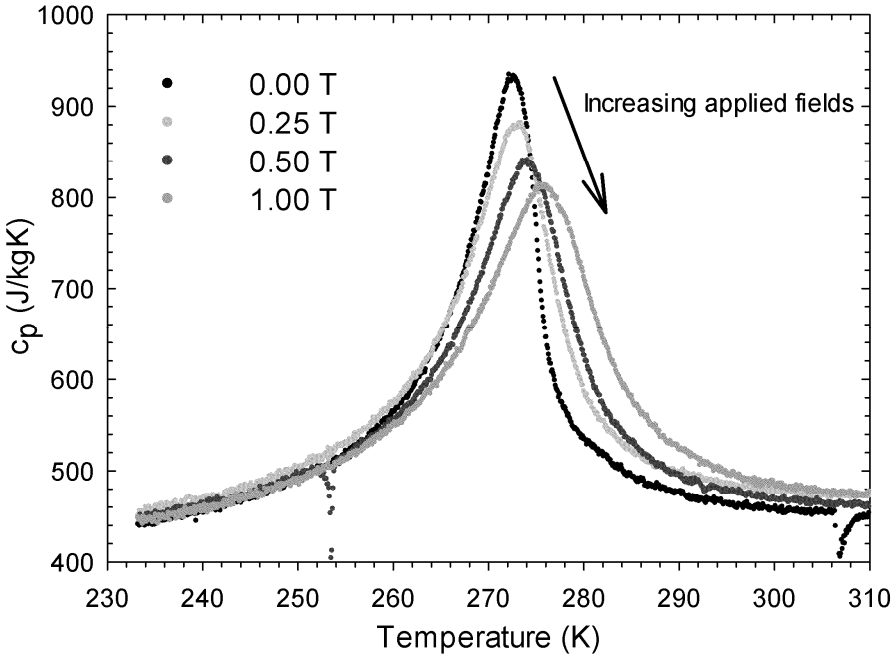


Figure 5. Heat capacity at constant pressure, $c_p$, in different applied fields, $\mu_0 H$. The two "spikes" observed in the data are purely instrumental.

## 5. CONCLUSIONS

In summary, we find that the magnetocaloric plate studied here with nominal composition $La(Fe_{0.851}Co_{0.066}Si_{0.083})_{13}$ presents a ferromagnetic-to-paramagnetic transition and a large volumetric magnetic entropy change upon application of a magnetic field. Several of the problems in using the $NaZn_{13}$-structured materials as magnetic refrigerants have been shown to have been resolved. Fabrication and preparation are resolved in that the production method of powder metallurgy has been shown to result in a plate with only small amounts of impurities. With regards to hysteresis, only a small thermal hysteresis is present in the material and no magnetic hysteresis. Issues not addressed in this paper are those of corrosion and brittleness, but we would like to add comments to these. The material does corrode quickly in pure water, but we have found that corrosion is slowed drastically by using an admixture of water and anti-freeze. Brittleness, however, is an issue, which should be addressed if the material series of $La(Fe,Co,Si)_{13}$ is to be used commercially as magnetic refrigerants.

## 6. ACKNOWLEDGEMENTS

Dr. Bente Lebech and research technician Jørgen Geyti are thanked for their invaluable help. The authors further acknowledge the support of the Programme Commission on Energy and Environment (EnMi) (Contract No. 2104-06-0032), which is part of the Danish Council for Strategic Research.

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