Stability of magnetocaloric $La(Fe_xCo_ySi_{1-x-y})_{13}$ in water and air

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Abstract

Stability of cobalt-doped lanthanum iron silicide, $La(Fe_xCo_ySi_{1-x-y})_{13}$ have been investigated under conditions required for magnetocaloric refrigeration. The XRD analysis revealed that both milled and non-milled samples stored in water loose a few Bragg peaks corresponding to the $NaZn_{13}$ phase of $La(Fe_xCo_ySi_{1-x-y})_{13}$. Samples stored in air show well-defined Bragg peaks similar to that of pristine material. The SEM-EDS of the milled and non-milled samples stored in water and air show an increased concentration of oxygen in the samples, particularly those treated with water. The course non-milled powders stored in air and water show sharp transitions at the Curie temperature T_C = 300K without large magnetization above the T_C. The milled, fine-particulate sample stored in air shows a slightly broadened transition at T_C, and that stored in deionized water for 14 days shows significantly broadened transition from 300K and retains large magnetizations above 400 K. This is indicative of relatively fast hydrolysis and removal of some or all of La, likely as hydroxide, from fine powders, leaving behind La-poor or, potentially, La-free Fe-Co-Si containing ferromagnetic residue with much higher Curie temperature. The non-milled course sample stored in water has sharper magnetic transition and higher magnetization hence it shows the highest entropy change among all 4 type of samples.

Introduction

Magnetocaloric refrigeration is an upcoming environmentally friendly cooling method which is based on magnetocaloric effect observed in ferromagnetic materials. In addition to its high efficiency, this promising cooling technology is an attractive alternative to vapor compression systems that employ harmful CFC and HCFC as working fluids [1]. The cooling efficiency in magnetic refrigerators is higher (the magnetic cooling efficiency can be reached up to 60% of a Carnot cycle, whereas it is only 5–10% for vapor compression refrigeration) even at a small scale, enabling the development of portable, battery-powered products [2]. Giant magnetocaloric effects are observed in materials that undergo a first-order magnetic transition (FOMT), because the FOMT is associated with an abrupt change in crystallographic lattice which enhances magnetocaloric effects (MCE) via a spin–lattice coupling [3, 4]. Pecharsky et. al reported 'Giant Magnetocaloric Effect' in $Gd_5Si_2Ge_2$ near room temperature [3, 4], an event that sparked worldwide interest in developing new kinds of magnetocaloric materials and magnetic

refrigeration systems. The first order phase transition materials also exhibit other extreme properties such as giant magnetoresistance and colossal magnetostriction at the phase transition temperature which can be used in many sensor and actuator applications [5-7]. Lanthanum iron Silicon with cobalt substitution is a potential magnetocaloric material that can be used in commercial magnetocaloric refrigerators due its low materials cost and comparable adiabatic temperature change upon application of magnetic field [8-10].
In this paper, we have investigated the stability of coarsely ground (non-milled) particles and milled fine particles under different conditions that are needed for optimal operation of magnetic refrigerator. Four different types of $La(Fe_{0.842}Co_{0.073}Si_{0.084})_{13}$ particles are characterized. These include two milled fine particle samples, one placed in air and water, similarly the other 2 non-milled samples placed in air and water. The coarse non-milled samples have particle size of about 50-100 microns and fine milled samples have particle size below 1 micron. These samples are characterized by comparison of XRD analysis, SEM, elemental composition, magnetization vs. temperature, magnetization vs. magnetic field and change in entropy vs. temperature for a magnetic field change of 5T. The non-milled coarse samples exhibit better magnetocaloric effect (MCE) when stored in water as compared to the one stored in air.

Experimental Details

Preparation of bulk $La(Fe_xCo_ySi_{1-x-y})_{13}$

The sample with a nominal composition of $La(Fe_{0.842}Co_{0.073}Si_{0.084})_{13}$ was prepared by arc-melting of elements under argon atmosphere. A total of 20 g of elements, taken in stoichiometric proportions, were melted together on a water-cooled Cu-hearth. The ingot was then re-melted four times and was turned over each time to achieve homogeneity. The total measured weight loss was less than 0.5 wt. %. The as-cast ingot was broken into smaller pieces, which were then wrapped within a tantalum-foil and sealed inside fused-silica tube under vacuum for further heat treatment. The Ingot pieces were annealed at 1050°C for one week followed by quenching in ice-cold water.

Ball milling to obtain submicron particles

To obtain the milled sample, the annealed pieces were crushed in an agate mortar inside an argon-filled glove box and sieved to a uniform particle size of 100µ or below. This powder was then ball-milled in hardened steel containers using a SPEX8000 mill. Milling was performed for 10 mins. in argon atmosphere and under dry conditions using a ball-to-powder ratio of approximately 1:1. After milling, powder was removed from the containers and used for characterization and magnetic measurements. Similar milling process has been used and reported for other rare-earth magnetic nanoparticles by us [11].

Results

SEM and EDS Analysis

Figures 1 is obtained utilizing Ultra High-Resolution Analytical FE-SEM SU-70 at the secondary electron image resolution of 5k at 5 kV. Figure 1 shows the SEM analysis of the samples. As it can be clearly seen in the Figure 1(d) more water is absorbed by milled sample as compared to the nonmilled sample stored in water. Milling increased the surface area and as a result milled sample had smaller particle allowing more water to react efficiently as compared to nonmilled

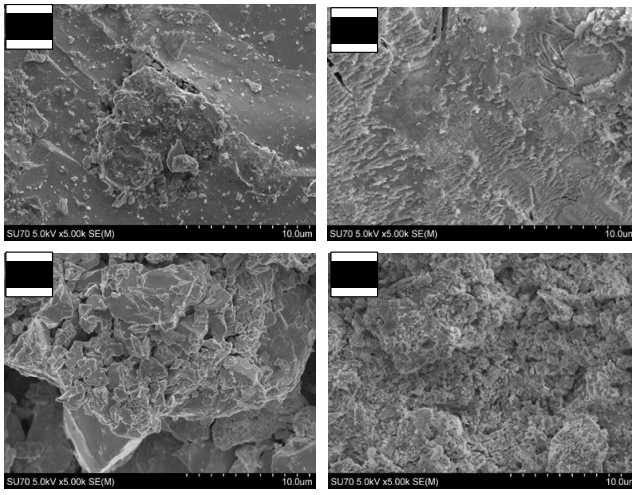

Fig. 1:SEM analysis of LaFeSiCo (a) Non-milled sample stored in air (b) Non-milled sample stored in deionized stored in water (c) Milled sample stored in air (d) Milled sample stored in deionized water for 14 days

(a)		
Elements	Wt%	At%
OK	1.7	6.2
SiK	3.15	6.6
LaL	19.8	8.4
FeK	69.6	73
CoK	5.81	5.8

(b)		
Elements	Wt%	At%
OK	5.58	19.2
SiK	3.38	6.27
LaL	17.6	6.6
FeK	68.28	63.7
CoK	4.86	4.3

(c)		
Elements	Wt%	At%
OK	3.28	12
SiK	2.51	5.1
LaL	19.4	7.9
FeK	69	70
CoK	7.5	5.6

(d)		
Elements	Wt%	At%
OK	8.59	26.7
SiK	2.6	4.61
LaL	18.97	6.8
FeK	62.33	55.5
CoK	7.5	6.33

Table 1: EDS analysis of $La(Fe_{0.842}Co_{0.073}Si_{0.084})_{13}$ (a) Non- milled sample stored in air (b) Non- milled sample stored in deoinized water for 14 days (c) Milled sample stored in air (d) Milled sample stored in deionized water for 14 days

sample particles. Table 1 presents the elemental composition of all four samples. Milled sample stored in air has the maximum amount of Oxygen that is from the contamination of the water.

XRD Analysis

PANalytical X'PertPro diffractometer is used to determine crystal structure of the samples. Samples began to lose peaks when contaminated with water as shown in Fig.2. Based on this X-Ray diffraction samples air Non-Milled sample show LaCo13 like structure but the lattice parameters are larger than LaCo13 compound. There is a huge peak at 55 deg which may arise from preferred orientation or an impurity that is susceptible to decomposition in air. Water Non-Milled sample show LaCo13 like structure but the lattice parameters are larger than LaCo13 compound. Except for the 55-degree peak rest of the pattern appears to be more or less similar to as-synthesized material.

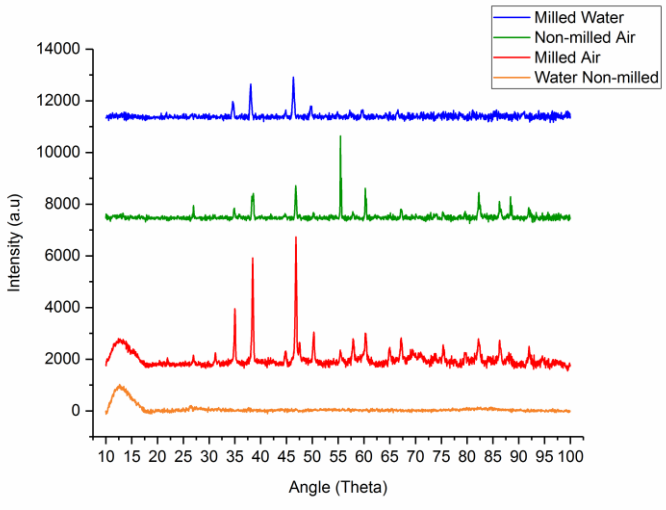

Fig.2: X-Ray diffraction patterns of milled and non-milled $La(Fe_xCo_ySi_{1-x-y})_{13}$ samples stored in water and air recorded using Cu K_α radiation

Magnetic measurements

Figure 3 presents the relationship between magnetization (emu/g) and

temperature (K) at an applied magnetic field of 0.01T. Both milled samples stored in air and water have broader transition temperatures around 300 K whereas, both non-milled samples stored in air and water have sharp transitions at 300 K. Milled sample that is stored in water has highest magnetization and retains large magnetization above 300 K. This is indicative of relatively fast hydrolysis and removal of some or all La as hydroxide from fine powders, leaving behind La-poor or, potentially, La-free Fe-Co-Si containing ferromagnetic residue with much higher Curie temperature.

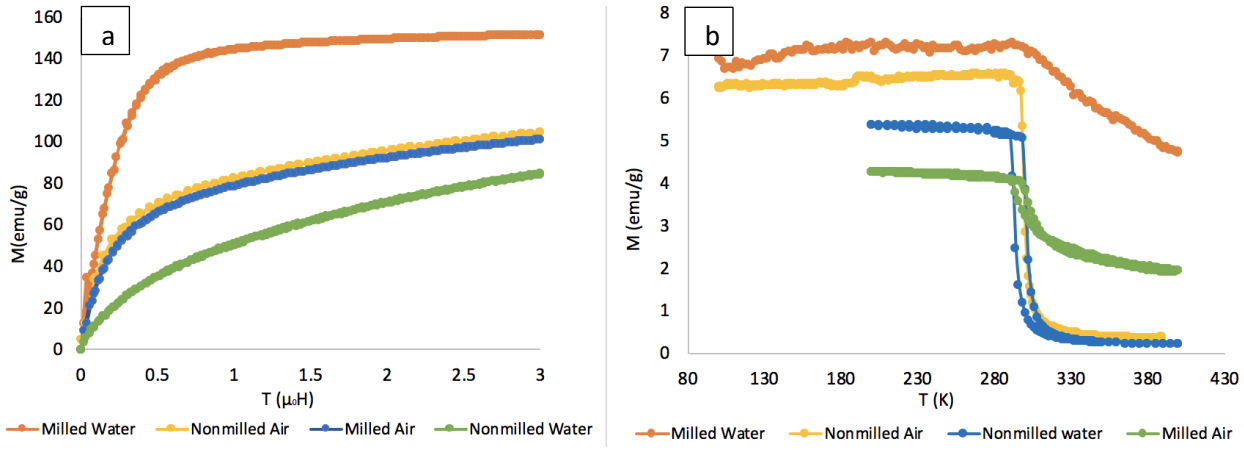

Fig. 3: Magnetic measurements of $La(Fe_xCo_ySi_{1-x-y})_{13}$ samples (a) Magnetization (emu/g) vs. Magnetic Field (T) at 300 K (b) Magnetization (emu/g) vs. Temperature (K) at 0.01 T

Figure 3(a) shows magnetization vs. magnetic field at 300K. Milled sample that is stored in water shows the highest saturation magnetization followed by both non-milled samples and milled sample stored in air. Non-milled sample stored in water has the highest relative permeability. Addition of water to both milled and non-milled samples increase magnetization compared to the samples stored in air as seen in Figure 3.

Entropy is one of the main parameters to characterize any magnetocaloric material. Based on the M-H curves, the magnetic entropy change can be calculated using the Maxwell's equation [3].

$$\Delta S = \int_o^H \mu 0 \left(\frac{\partial M}{\partial T}\right) dH$$

Fig. 4 shows the temperature dependence of the change in magnetic entropy for the characterized samples for a magnetic field change of 3T. The change in entropy is highest closer to the magnetic transition temperature like other magnetocaloric materials where ferromagnetic to paramagnetic phase transitions will show the maximum entropy change [4].

The curve of the non-milled sample store in water shows the maximum change in magnetic entropy value of 11 J $Kg^{-1}K^{-1}$ near 300 K while the milled sample stored in water has the lowest entropy change. Maximum magnetic entropy change of ΔS_M (T, H) as function of temperature of $LaFe_{11.6-x}$ Co_x $Si_{1.4}$ compounds (x = 0.5) has maximum entropy of ~7.5 J/Kg [12]. LaFeSiCo milled and

nonmilled sample stored in air shows almost same delta S except around 292 K. As shown in Fig. 3(a) Magnetization vs. Magnetic Field of milled and nonmilled sample stored in air shows similar curve at 300 K that can also be seen from the Fig. 4 change in entropy of these two samples at 300 K is almost equivalent.

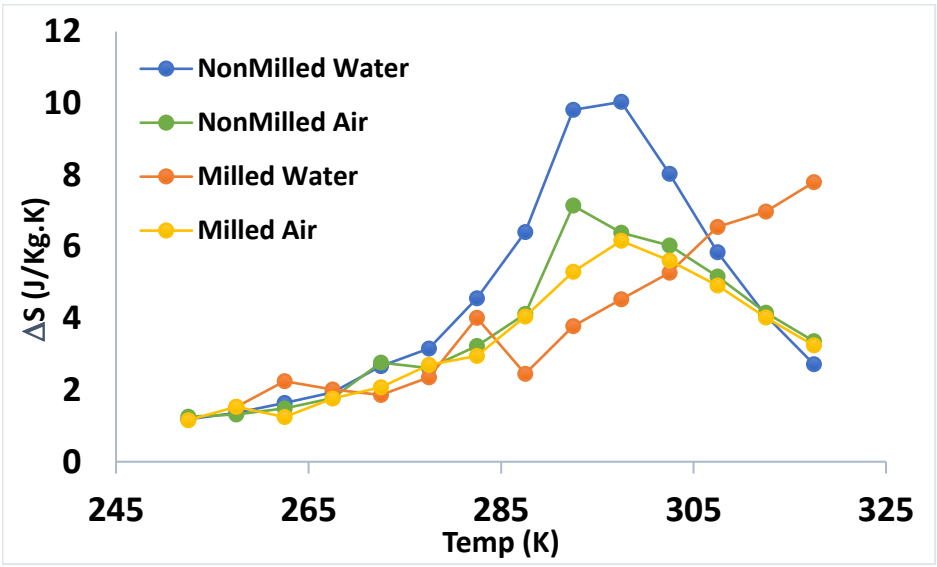

Fig.4: ΔS vs. Temperature for a magnetic field change of 3T

Discussion

Milling process has significantly broadened the transition hence milled sample stored in water has the lowest entropy change. Magnetic refrigerator is a complex structure that includes fabrication of magneto-caloric material bed. This process requires the formulation of powder of MCM. This magnetocaloric bed when in contact with water might oxidize the material. Addition of water to both milled and non-milled samples has increased the magnetization which may be due to formation of Fe_3O_4. The increase in magnetization in water stored sample has resulted in higher entropy change. In a magnetic cooling device water can be used in as a heat transfer fluid for efficient transfer of heat from the magnetocaloric material to the heat exchanger.

Conclusions

It can be concluded that the course non-milled samples contain larger particles and resulted in sharper transition. Water added to the milled sample leads to hydrolysis and removal of some of the La as hydroxide from fine powders, leaving behind La-poor Fe-Co-Si containing ferromagnetic residue of possibly Fe_3O_4 or $CoFe_2O_4$ with much higher Curie temperature as follows from the absence of the large magnetization beyond 300K. The course non-milled particles show much greater stability and sharper magnetic transition when stored both in air and water. The course crushed sample stored in water has sharper magnetic transition and higher magnetization hence it shows the highest entropy change among all 4 types of samples.

Addition of water to the cobalt doped Lanthanum Iron Silicon has increased the magnetization which has resulted in the enhanced entropy change in the non-milled sample. Whereas milling process has reduced the entropy change due to broadened transition temperature and reduced magnetization compared to non-milled samples in e $La(Fe_{0.842}Co_{0.073}Si_{0.084})_{13}$ system.

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