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Magnetocaloric effect, thermal conductivity, and magnetostriction of epoxy-bonded La($Fe_{0.88}Si_{0.12}$) $_{13}$ hydrides

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Abstract. Magnetic materials with large magnetocaloric effect are significantly important for magnetic refrigeration. La($Fe_{0.88}Si_{0.12}$)$_{13}$ compounds are one of the promising magnetocaloric materials that have a first order magnetic phase transition. Transition temperature of hydrogenated La($Fe_{0.88}Si_{0.12}$)$_{13}$ increased up to room temperature region while keeping metamagnetic transition properties. From view point of practical usage, bonded composite are very attractive and their properties are important. We made epoxy bonded La($Fe_{0.88}Si_{0.12}$)$_{13}$ hydrides. Magnetocaloric effect was studied by measuring specific heat, magnetization, and temperature change in adiabatic demagnetization. The composite had about 20% smaller entropy change from the hydrogenated La($Fe_{0.88}Si_{0.12}$)$_{13}$ powder in 2 T. Thermal conductivity of the composite was several times smaller than La(Fe,Si)$_{13}$. The small thermal conductivity was explained due to the small thermal conductivity of epoxy. Thermal conductivity was observed to be insensitive to magnetic field in 2 T. Thermal expansion and magnetostriction of the composite material were measured. The composite expanded about 0.25% when it entered into ferromagnetic phase. Magnetostriction of the composite in ferromagnetic phase was about 0.2% in 5 T and much larger than that in paramagnetic phase. The composite didn't break after about 100 times magnetic field changes in adiabatic demagnetization experiment even though it has magnetostriction.

1. Introduction

Magnetic refrigeration makes use of the magnetocaloric effect (MCE). Because of the reversibility of entropy changes, magnetic refrigeration can achieve a very high thermodynamic efficiency. Magnetic refrigeration systems can be environmentally friendly, quiet, and potentially more efficient than conventional gas expansion systems. Magnetic materials with large magnetocaloric effect are significantly important for magnetic refrigeration. Gadolinium and Gd-based alloys are the benchmark MCE material in room temperature region.

La(Fe,Si)$_{13}$ compounds are one of the promising magnetocaloric materials that have a first order magnetic transition (FOMT). This material is attractive because of large MCE and abundance. La(Fe,Si)$_{13}$ hydrides is widely studied because hydrogenation of La(Fe,Si)$_{13}$ rises the transition temperature up to room temperature region, keeping the magnetic transition as first order one. La(Fe,Si)$_{13}$ hydrides are brittle and available only in powder or small pieces and it is necessary to use some processing to make required forms. Polymer-bonded method was tried to make composite materials from $La(Fe,Si)_{13}$ and $La(Fe,Mn,Si)_{13}H_x$ [1,2]. From view of designing of refrigerator with compositional magnetocaloric materials, thermal conductivity and other properties are also important issues.

In this study, epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides were fabricated and their thermal and magnetocaloric properties were investigated. Magnetocaloric effect was studied by measuring specific heat, magnetization, and temperature change in adiabatic demagnetization. Thermal conductivity, thermal expansion and magnetostriction were also measured.

2. Experiments

Bulk $La(Fe_{0.89}Si_{0.11})_{13}$ flakes were prepared from melt by a single-roll process. After homogenization process, the $La(Fe_{0.88}Si_{0.12})_{13}H_x$ material was hydrogenated. The hydrogenated powder was sieved, particle size used for epoxy composite was between 38 and 75 μm. Compacts for thermal conductivity measurement were prepared as follows; the hydrogenated powder was mixed with 3 wt% epoxy and compacted at about 0.1 GPa. Plates with size of about 20 mm length and 5 mm thick were obtained. Density of the epoxy bonded composite was determined as 6.4 g/cm^3 by Archimedes method. Figure 1 shows the photograph of the compact rectangular parallelepiped. The hydrogenated powder used for thermal expansion and magnetostriction measurements was prepared in another run so that the hydrogen composition was different from that for MCE and thermal conductivity measurements. The compact for thermal expansion and magnetostriction measurements were made using 4 wt% epoxy.

Specific heat was measured with Quantum Design PPMS in magnetic fields of 0 and 2 T. Magnetization curves and temperature dependence were measured with Quantum Design MPMS. The measurements of the thermal conductivity were performed by a steady-state method with a homemade apparatus in 0 and 2 T. The temperature gradient was measured between two points on the rod sample when defined amount of heat flux was passing through the sample. The thermal conductivity was calculated with the temperature gradient, corresponding heat flux, and cross section of the rod sample in terms of Fourier's law. Adiabatic demagnetization experiment was performed with homemade apparatus that has a superconducting magnet in persistent mode. The $La(Fe_{0.88}Si_{0.12})_{13}H_x$ compact suspended in a vacuum chamber with fine Kevler thread was pushed out and pulled into high magnetic field in several seconds keeping adiabatic condition. Temperature was measured with a Si diode temperature sensor. Thermal expansion and magnetostriction were measured using a homemade capacitive dilatometer that was installed in Quantum Design PPMS [3].

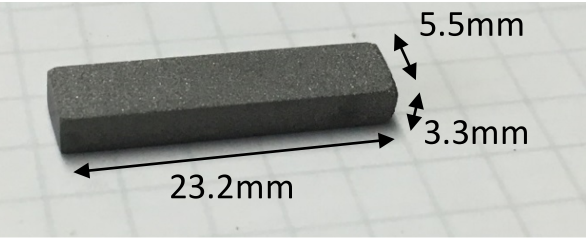

Figure 1. Photograph of the epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides rod for thermal conductivity measurement.

3. Results and Discussion

3.1. Specific heat

Figure 2 shows the specific heat of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides in 0 and 2 T. Specific heat has a sharp peak at the ferromagnetic transition temperature, 332 K. Hydrogen concentration dependence of magnetic transition temperature for $La(Fe_{0.88}Si_{0.12})_{13}H_x$ was reported in Ref. [4]. Transition temperature increased in proportion with hydrogen concentration. From this relation, hydrogen concentration of our compact was estimated as $La(Fe_{0.88}Si_{0.12})_{13}H_{1.63}$. The peak temperature was increased by 7 K with 2 T magnetic field. The peak of specific heat is suppressed in height and broadened a little by applying magnetic field. This behaviour is typical for FOMT materials such as $Gd_5(Si_xGe_{1-x})_4$ and $La(Fe_{0.88}Si_{0.12})_{13}$. The maximum heat capacity in 0 T was near 1850 J/kgK that was close to bulk $La(Fe_{0.88}Si_{0.12})_{13}$ hydride.

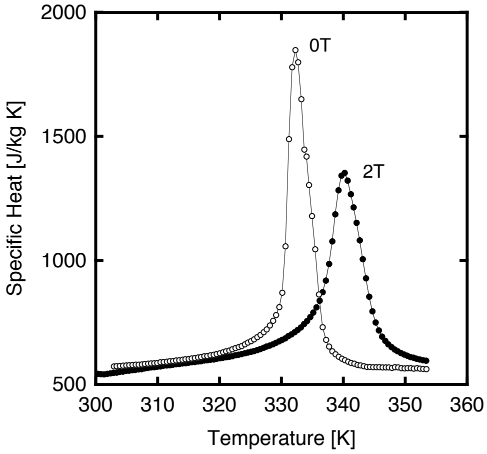

Figure 2. Specific heat of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides in 0 and 2 T.

3.2. Magnetization

Magnetization of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides was shown in Fig. 3 as functions of temperature. It is clearly shown in small magnetic fields that magnetization represent kinks at temperatures corresponding to FOMT. Magnetization of ferromagnetic phase saturated in about 1 T.

Magnetic entropy change (ΔS) was calculated using Maxwell's relation as $\Delta S = \int_0^H \left(\frac{\partial M}{\partial T}\right) dH$. Figure 4 shows ΔS of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides as functions of temperature. The maximum $|\Delta S|$ of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides was 17.2 J/kgK which is larger than that of polymer bonded $La(Fe,Mn,Si)_{13}H_x$ in Ref. [2]. The temperature region with large ΔS was expanded to higher temperature by higher magnetic field, keeping the maximum ΔS as almost constant. This behaviour of ΔS with various magnetic fields is often observed in FOMT materials.

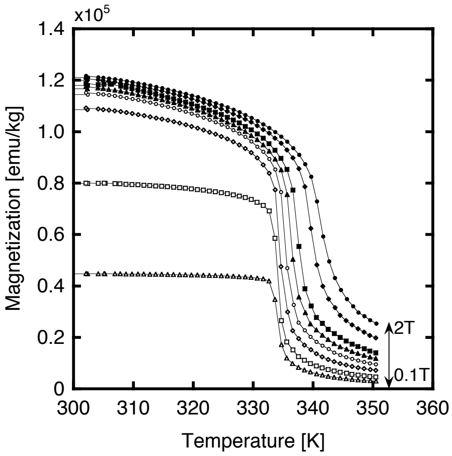

Figure 3. Magnetization of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides in 0.1, 0.2, 0.4, 0.6, 0.8, 1, 1.5, and 2 T.

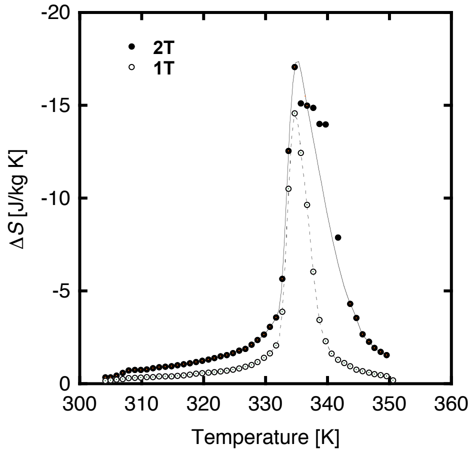

Figure 4. Entropy change of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides

3.3. Entropy-Temperature diagram

The total entropy (*S*) was obtained by integrating specific heat divided by temperature (*C*/*T*) with respect to temperature at constant magnetic field, as $S(T,H) = \int_0^T \frac{C(T,H)}{T} dT$, where *C*(T, H) is the specific heat at a constant field *H*. The *S*(*T*, *H*) was determined so that Δ*S* obtained from the specific heat and the Δ*S* obtained from magnetization were consistent with each other. Figure 5 gives the entropy-temperature (*S*–*T*) diagram of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides. Entropy increases rapidly at the transition temperature because of FOMT.

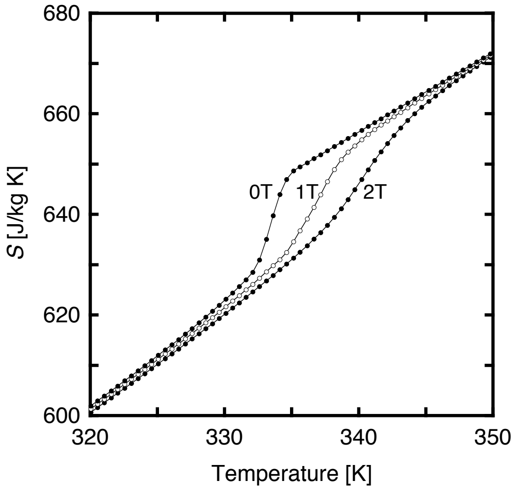

Figure 5. Entropy-Temperature diagram of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides in 0, 1, and 2 T.

3.4. Temperature change in Adiabatic demagnetization

Figure 6 represents the temperature change (Δ*T*) in adiabatic demagnetization and magnetization. It was confirmed that temperature changes almost coincided in magnetization and demagnetization processes (not shown in Fig. 6). Abscissa of Fig. 6 represents the starting temperature of demagnetization. Maximum temperature changes of 3.5 and 5.5 K were obtained at 337 and 339 K with 1 and 2 T, respectively. Those temperature changes were in good agreement with those estimated from the *S*–*T* diagram. The composite maintained its shape after about 100 times magnetic field changes in adiabatic demagnetization experiment even though it has magnetostriction as explained in section 3.6.

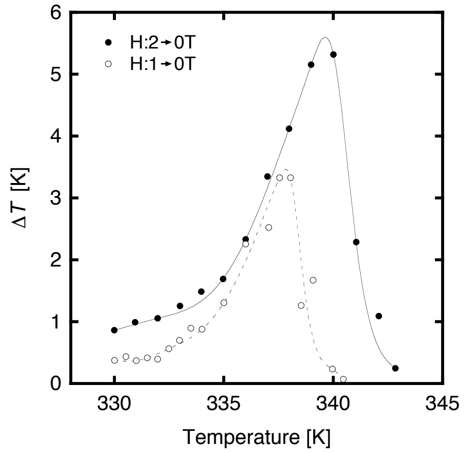

Figure 6. Adiabatic temperature change of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides . Abscissa represents the starting temperature of demagnetization.

3.5. Thermal conductivity

In order to discuss heat transfer between fluid and magnetic material, thermal conductivity of epoxy bonded compact is important. Figure 7 shows thermal conductivity of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides in 0 T. The difference of thermal conductivity in 0 and 2 T was within our experimental error. As shown in the Fig. 7, thermal conductivity of our epoxy bonded compact is about three times smaller than that of bulk [5]. The thermal conductivity due to electron was estimated as 60% of total κ using Wiedeman-Franz law and electric conductivity for $La(Fe_{0.88}Si_{0.12})_{13}H_{0.4}$ [6]. It looks to be reasonable that our epoxy bonded compact had smaller thermal conductivity than that of bulk. Because epoxy is an insulator and the thermal conductivity of epoxy is about two order of magnitude smaller than $La(Fe_{0.88}Si_{0.12})_{13}$, 3 wt% epoxy caused significant decrease in thermal conductivity of composite material. Radulov et al. made $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides polymer composite in various processes and measured thermal conductivity [2]. Thermal conductivity of the compact was ~5 W/Km at around 300 K. Low thermal conductivity of our compact might be attributed to inclusion of voids so that detailed study on synthesis pressure, particle size, and adhesion are necessary to improve thermal conductivity of epoxy bonded magnetocaloric material.

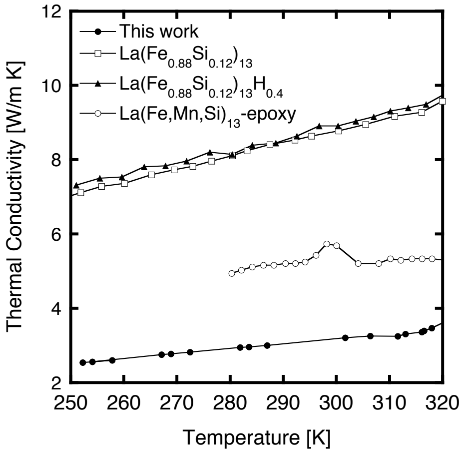

Figure 7. Thermal conductivity of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides in 0 and 2 T. That of bulk $La(Fe_{0.88}Si_{0.12})_{13}$ is plotted form literatures [2, 6]

3.6. Thermal expansion and magnetostriction

Our epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides expanded about 0.25% when it entered into ordered phase in 0 T as shown in Fig. 8. Thermal hysteresis was not significant. The expansion ($\Delta L/L$) of bulk $La(Fe_{0.88}Si_{0.12})_{13}$ was measured as about 0.3% at the transition by X-ray diffraction [7]. $\Delta L/L$ of our compact did not change so rapidly as bulk. Epoxy possibly made abrupt volume change smooth.

Figure 9 shows magnetostriction of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides as functions of squared magnetic field in ferromagnetic phase, around transition temperature, and paramagnetic phase. In all temperatures, the epoxy bonded compact expands by magnetic field. Hysteresis wasn't observed. Large magnetostriction was observed only around transition temperature and rapidly changed from 0 to 2 T. In paramagnetic phase, magnetstriction is in proportion to squared field. At well below transition temperature, magnetostriction shows saturation. The composite maintained its shape after thermal expansion and magnetostriction measurements.

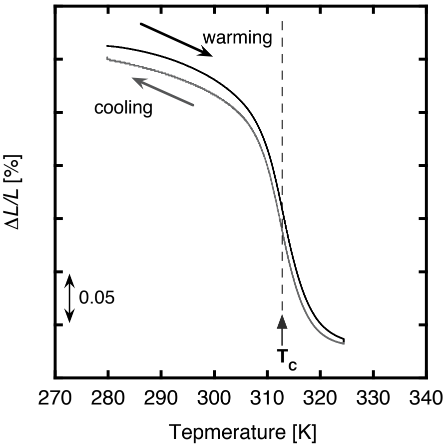

Figure 8. Thermal expansion of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides in 0 T.

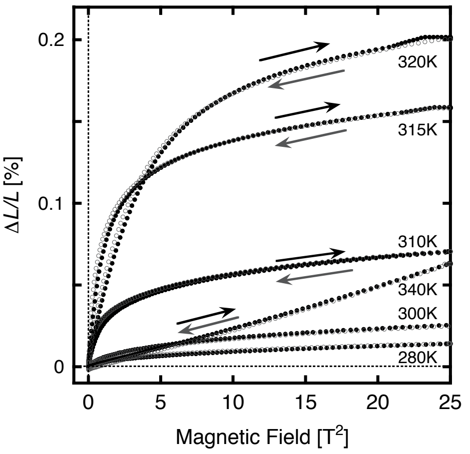

Figure 9. Magnetostriction of epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides. Magnetostriction is plotted as functions of squared magnetic field.

4. Summary

We made epoxy bonded $La(Fe_{0.88}Si_{0.12})_{13}$ hydrides. Magnetocaloric effect was studied by measuring specific heat, magnetization, and temperature change in adiabatic demagnetization. The epoxy bonded compact maintained sharp magnetic transition so that have large magnetocaloric effect. Entropy-temperature diagram was obtained from these measurements. Adiabatic temperature change in adiabatic demagnetization was observed and coincided with that estimated from entropy-temperature diagram. Thermal conductivity was several times smaller than bulk $La(Fe_{0.88}Si_{0.12})_{13}$ due to low thermal conductivity of epoxy adhesion. The compact expanded 0.25% when it entered into ferromagnetic phase. Magnetostriction was largest around the transition temperature.

5. Acknowledgments

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