Magnetocaloric Effect of Micro- and Nanoparticles of Gd_5Si_4

S. M. Harstad,[1] A. A. El-Gendy,[1,2] S. Gupta,[3] V. K. Pecharsky,[3,4] and R. L. Hadimani[1]

[1]Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, USA

[2]Department of Physics, University of Texas El Paso, USA

[3]Ames Laboratory, Division of Materials Science and Engineering, U.S. Department of Energy, USA

[4]Department of Materials Science and Engineering, Iowa State University, USA

ABSTRACT

Materials exhibiting large magnetocaloric effect (MCE) at or near room temperature are critical for solid-state refrigeration applications. The MCE is described by a change in entropy (ΔS_M) and/or temperature (ΔT_{ad}) of a material in response to a change in applied magnetic field. Ball milled materials generally exhibit smaller ΔS_M values compared to bulk; however, milling broadens the effect, potentially increasing the relative cooling power (RCP). The as-cast Gd_5Si_4 is an attractive option due to its magnetic transition at 340 K and associated magnetocaloric effect. Investigation of effect of particles size and transition temperature in the binary material, Gd_5Si_4, can lead to development of functionally graded bulk material with higher MCE and RCP than the traditional bulk materials. A two-step ball-milling process, in which coarse powder of Gd_5Si_4 was first milled with poly(ethylene glycol) followed by milling in heptane was used to produce fine particles of Gd_5Si_4 that showed a broad distribution in particle size. Magnetic measurement on the milled sample obtained after washing with water show decrease in Curie temperature and significant broadening of magnetic transition. Compared to bulk Gd_5Si_4, the maximum MCE of the milled samples is also reduced and shifted down by close to 30 K, but the MCE remains substantial over a broader temperature range. The RCP of both milled samples increased 75% from the bulk material.

INTRODUCTION

Recently there has been significant effort in research directed at materials with a magnetocaloric effect (MCE) near room temperature for refrigeration applications [1]. This effort is fuelled by the opportunity for increased energy efficiency over that of conventional vapor compression refrigeration cycle. The MCE is described by a change in entropy (ΔS_M) and/or temperature (ΔT_{ad}) of a material in response to an applied magnetic field. The giant magnetocaloric effect is seen in materials that exhibit a first order structural phase transition but with the drawback that these materials also experience hysteresis loss when cycled through transition temperature and magnetic field. The somewhat lesser performing second order phase transition materials show an MCE over a slightly larger temperature range, and do not suffer hysteresis losses but possess lower values of ΔS_M and ΔT_{ad}. One of the main goals of research on magnetocaloric materials is to increase the MCE or the temperature range of second order materials [2], [3]. To this end, a simple and effective process of ball milling the magnetic materials is often employed which, generally results in powders that exhibit smaller absolute maximum ΔS_M values than their bulk material counterparts as reported by a few research groups recently. However, this reduction in ΔS_M is accompanied by the extension of the MCE over a larger range of temperatures, potentially increasing the relative cooling power (RCP) of the material which has been reported in several systems [4]–[7]. When examining potential systems for magnetic refrigeration one of the main concerns is the material's performance near room temperature as most commercial cooling demands are for near room temperature applications. The Gd_5Si_4 and a few of its derivatives provide an attractive option because of their strong magnetostructural transition near room temperature [8]–[14]. It is important to study the properties of $Gd_5(Si_xGe_{1-x})_4$ in order to improve the performance of magnetic refrigerators. $Gd_5(Si_xGe_{1-x})_4$ also exhibits other unusual properties at the first order phase transition such as giant magnetoresistance of $\Delta R/R = 25\%$ [15]–[17] colossal magnetostriction of the order of 10,000 ppm [18]. These extreme properties occur close to room temperature for compositions in the range $0.4 < x < 0.575$ which can be utilized in various engineering applications. These properties can be controlled by variation of temperature, magnetic field and composition which offer versatility to potential applications. There are few journal publications on thin films and nano structures of $Gd_5(Si_xGe_{1-x})_4$. Magnetocaloric thin films have the potential to be used in cooling the integrated circuits. Magnetocaloric thin films can also be used in various MEMS applications. Few researchers in the magnetocaloric community attempted to prepare rare-earth thin films of

$Gd_5(Si_xGe_{1-x})_4$ but have failed [19], [20] because of high melting points of the compounds (exceeding 1700° C), incongruent melting, and extreme difficulties in controlling oxygen content during and after deposition. Hadimani et al. [21]–[23] showed high probability of success, even though the prepared films contained multiple phases. Importantly, the monoclinic $Gd_5Si_2Ge_2$ phase is expected to exhibit a magnetostructural transition similar to the bulk has been identified. Earlier unsuccessful attempts of depositing these films were based on pulsed laser deposition (PLD) using nanosecond laser and sputtering. PLD of metals give rise to particulate deposition hence, the thin films of Gd_5Si_4 also showed particulate deposition. We therefore were initially interested in the development of nanoparticles of Gd_5Si_4 in order to fully characterize the structures deposited during PLD [24]. After the results on nanoparticles were published, there was a significant interest in the application of these ferromagnetic nanoparticles for biomedical, energy harvesting and high frequency electromagnetic shielding applications[25]–[30]. The focus of this work is to investigate the effect of processing of bulk powder by ball milling on the magnetocaloric response of Gd_5Si_4 with specific interest on the response near room temperature.

EXPERIMENTAL DETAILS

A polycrystalline sample of Gd_5Si_4 was synthesized via arc-melting the stoichiometric mixture of commercial grade Gd (99.97%) and Si (99.999%) in an argon atmosphere. The sample was re-melted six times, turning over each time to ensure homogeneity. Using commercial grade Gd leads to the formation of small amounts of Gd_5Si_3 and GdSi impurities in the predominantly Gd_5Si_4 matrix. To obtain sub-micrometer particles of Gd_5Si_4, the as-cast bulk material was first ground in an agate mortar and screened to eliminate particles larger than 53 μm. Further reduction in the particle size was achieved by high-energy ball-milling of the powder in a SPEX 8000M mill using stainless steel container and milling media. The milling procedure used a powder to ball weight ratio of 5:1 with 2 balls of 11 mm diameter and 4 balls of 4 mm diameter. 10 wt% poly(ethylene glycol) (PEG) (molecular weight-8000 Da) was added to the Gd_5Si_4 powder to act as a surfactant during milling. A two-step milling process was used in which the powder and PEG mixture was first milled for 1 h at which point the milling was interrupted and 5 ml of heptane was added to the vial. The milling was then continued for another 1h for sample S1 and 2 h for S2. Shorter milling periods were chosen to maintain crystallinity as extended milling results in amorphous particles and low magnetization [31]. After milling is complete, the milling container is opened inside a glove box equipped with solvent-absorption system. The container is allowed to sit until most of the heptane evaporates. Any remaining heptane is then removed under vacuum. PEG was removed by washing the sample with deionized water.

The magnetic properties of the samples were measured using a vibrating sample magnetometer (Versalab, Quantum Design). Morphological characteristics were studied with scanning electron microscopy (Hitachi SU-70).

RESULTS

The x-ray diffraction analysis of as-cast sample shows formation of Gd_5Si_4 with orthorhombic (space group: Pnma) structure along with minor amounts of Gd_5Si_3 and GdSi. Despite careful manipulation of the starting elements and multiple re-melting of as-cast button, pure Gd_5Si_4 could not be obtained. It is most likely that small amount of non-metal impurities present in the commercial grade Gd leads to high relative stability of parasitic secondary phases. After the first hour of ball milling, the sample consisted of flakes that coated the media and walls of the vial indicating that the PEG was well integrated with the Gd_5Si_4 powder. Upon milling with heptane and subsequently drying under vacuum, the powder appeared to have very large surface area and fine particle size which was maintained after removal of PEG. The particles were examined using SEM to determine size and morphology (Fig. 1). Milling under these conditions produced particles that have a large size distribution with some particles larger than 1 micron. Increased milling time shows a higher percentage of smaller particles; however, large particles over 1 μm are still present. Most particles have a plate-like shape which may be due to preferential shearing along the slabs in the Gd_5Si_4 crystal structure [32].

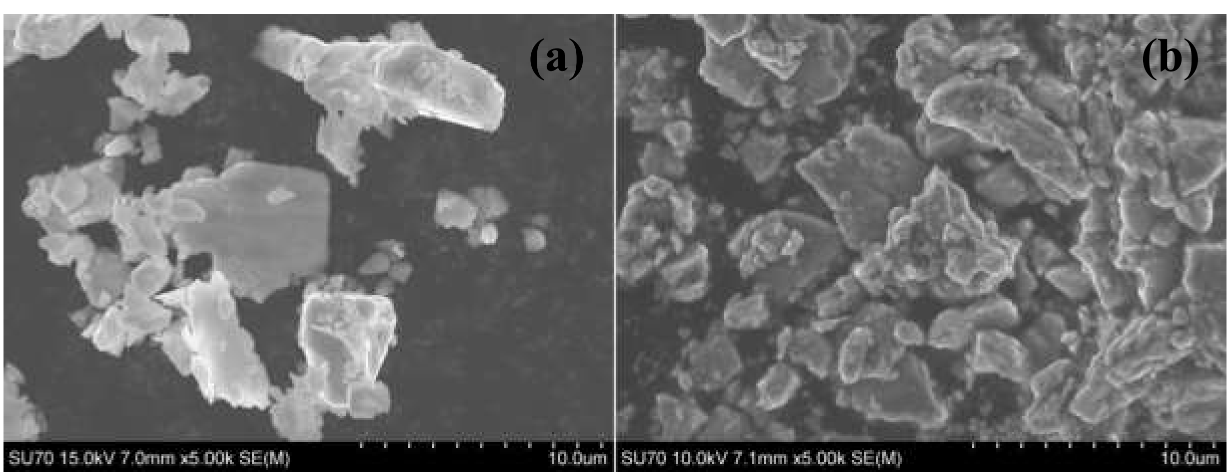

Figure 1: SEM images of (a) 2 hour and (b) 3 hour high energy milled nano/micro particles of Gd_5Si_4

Fig. 2 shows the magnetization as a function of temperature for the milled samples, S1 and S2, as well as bulk Gd_5Si_4. Both milled samples show ferromagnetic behavior below 330 K with a noticeable transition to paramagnetic phase occurring as temperature increases. Derivative of magnetization show that the particles have broad range of transition temperature and bulk has a transition temperature in a narrow range.

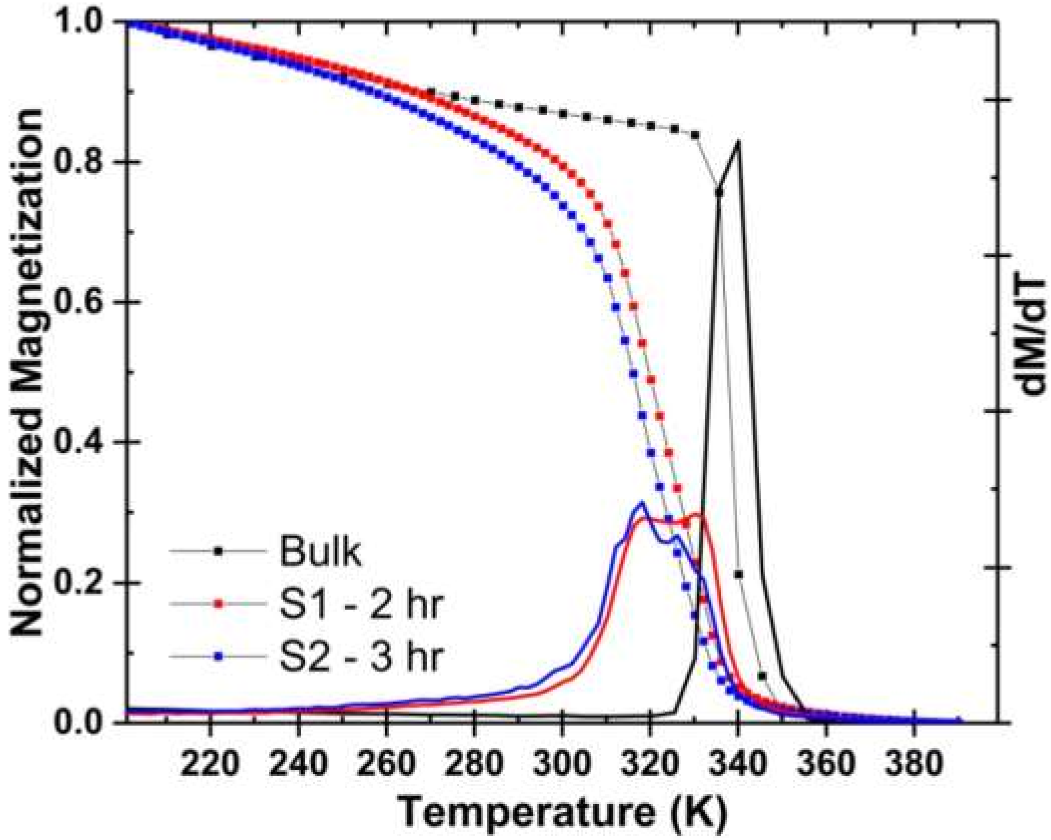

Figure 2: Magnetization as a function of temperature at an applied magnetic field of 100 Oe.

Fig. 3 shows hysteresis graphs in a magnetic field range of -30 kOe to 30 kOe for 2h and 3h milled nanoparticles of Gd_5Si_4 at 300 K. Inset is the magnified part of the hysteresis graph at the origin showing coercivity less than 50 Oe for 2h milled samples and less than 5Oe for 3h milled sample. The large variation in the magnetic moment was because of the presence of high amount PEG in the particles. Although PEG was washed away but for 3h milled sample, it was difficult to wash all the PEG away and large amount retained back in the sample.

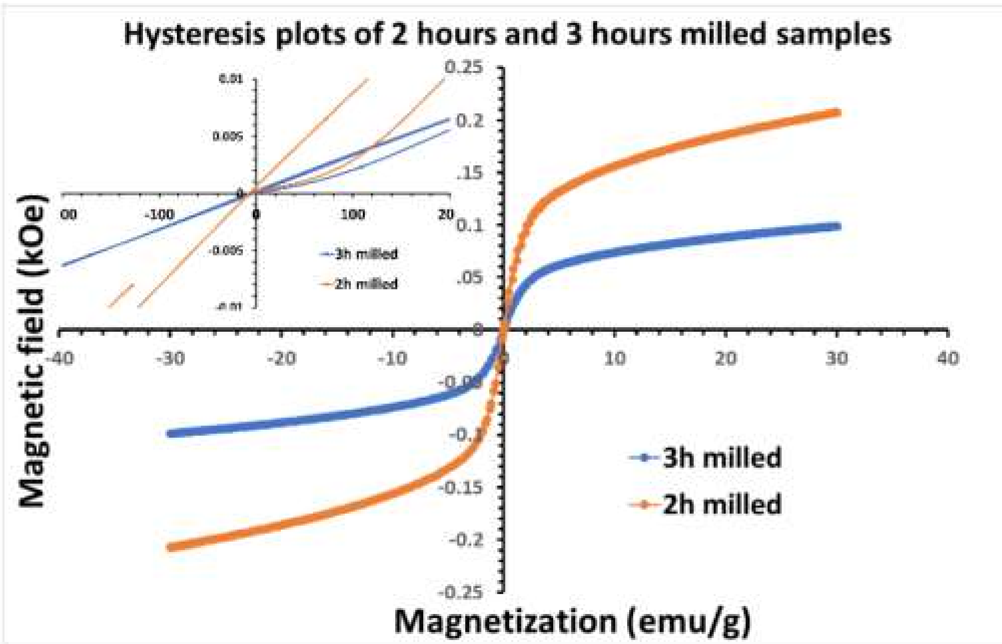

Figure 3: Magnetization as a function of magnetic field for 2h and 3h milled nanoparticles of Gd_5Si_4 at 300K. Inset is the magnified part of the hysteresis graph at the origin showing coercivity less than 50Oe.

Fig. 4 shows magnetization (M) isotherms in the range of 0-30 Oe that were collected from 210 K-390 K in order to calculate the magnetic entropy change via the Maxwell relation [10]

$$\Delta S_M = \int_0^H \frac{\delta M}{\delta T} dH \qquad [1]$$

where T is the absolute temperature and H is the applied magnetic field. The magnetocaloric effect is calculated using change in entropy for a change in magnetic field at a specific temperature using [1] are shown in Fig. 5. Temperature dependence of magnetization in Fig. 3 shows an early onset and smooth magnetic transition in the ball-milled samples indicating a distribution of Curie temperatures in the powder.

The ball-milled samples exhibit a subdued magnetocaloric response with a ΔS_M of 3 J/kgK that has broadened over a large temperature range. The peak ΔS_M value has also shifted to a lower temperature in the milled samples. This shift follows the same trend as the magnetic transition temperature in ball milled Gd_5Si_4. Increased milling time further reduces the transition temperature as well as the peak value of ΔS_M. There is a small decrease in ΔS_M with increased milling time but little impact on further broadening of the response peak.

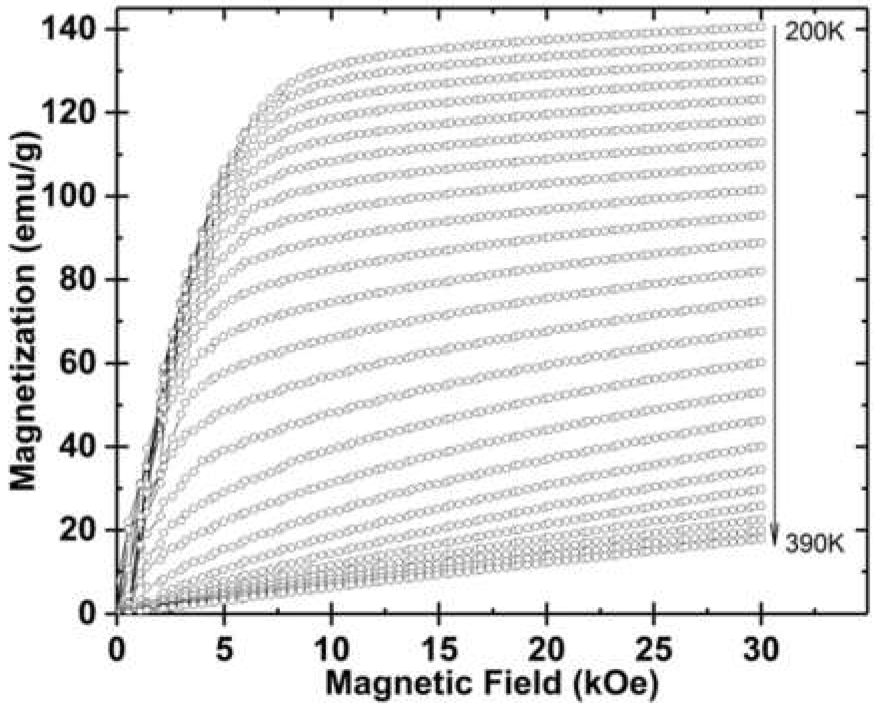

Figure 4: Magnetization as a function of magnetic field from 0-30 kOe for isotherms ranging from 200 K to 390 K. Isotherms of temperature above transition temperature are straight line showing paramagnetic behavior.

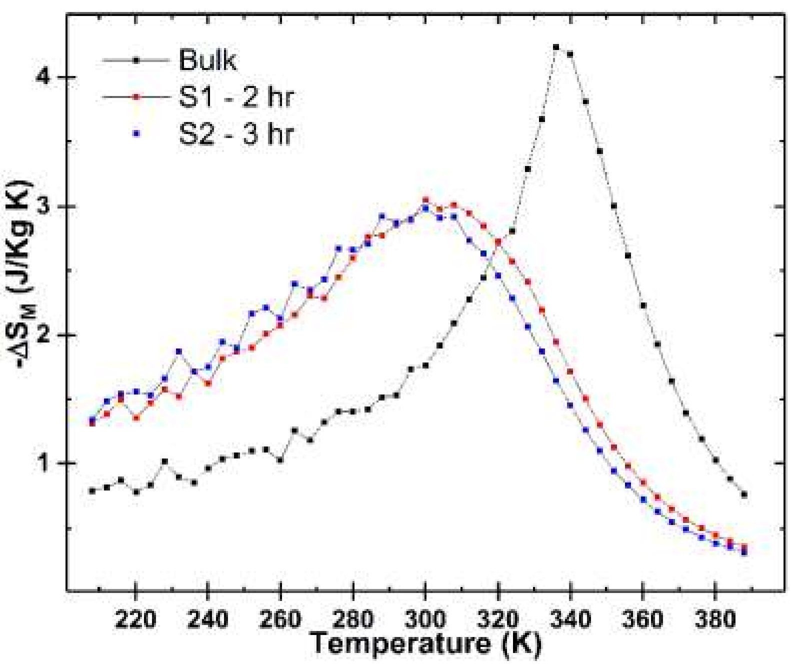

Figure 5: Magnetic entropy change vs temperature for bulk Gd_5Si_4 and both milled samples.

DISCUSSION

Ball-milling Gd_5Si_4 reduces the temperature at which the material undergoes its magnetostructural transition. The transition temperature of the bulk material is ~335 K and is reduced to about 320 K for milling times of 2 and 3 hours similar to previous reports in thin films [23]. As the particle size decreases, magnetic disorder at the surface has a larger influence on the magnetic ordering of the particle [4], [5]. In the case of ball-milling where particle and grain sizes are reduced, the magnetic transition is smoothed out over a range of temperatures which is observed in Fig. 2 and is in agreement with previous literature [33], [34]. In the bulk sample the structural transition causes a rather sharp peak in the ΔS_M curve that is centred on the transition temperature. However, in the milled samples we see that the peak change in entropy occurs nearly 15 K below the transition and remains substantial as temperature decreases. In both samples the spectrum of transition temperatures is expressed as a broad transition that translates to a very broad peak in ΔS_M as each size range of particles contributes to the whole at a specific temperature. This broadening gives rise to a much larger RCP in the milled samples when compared to the base material which confirms previous report by Blázquez *et al.*[4]. Using the standard full width at half maximum method for calculating cooling power the relative cooling power of both milled samples is ~340 J/kg; a 75% increase from the 200 J/kg provided by bulk Gd_5Si_4 material.

CONCLUSION

Gd_5Si_4 was ball-milled using PEG as a surfactant and heptane as a liquid processing agent. The resultant powder was sub-micron, maintained crystallinity and the magnetic transition temperature was reduced to 320 K from the bulk value of ~340 K. The MCE was slightly suppressed as expected but remains substantial and nearly constant over a wide temperature range between ~280 K and ~320 K with peak values occurring at room temperature, 295 K-300 K. Ball-milling Gd_5Si_4 is a viable route to producing coolant material with good performance at room temperature. Functionally graded Gd_5Si_4 with improved cooling performance can be developed from additive manufacturing using the nanoparticles reported in this paper.

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